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ESSENTIALS OF CHEMISTRY

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SAMUEL USHER
176 TO 184 HIGH STREET
BOSTON, MASS.

PREFACE.

The interest aroused by the introduction of laboratory science into secondary schools, a decade and a half ago, brought out a number of text-books of Chemistry. Although most of these books had directions for laboratory work scattered through the descriptive matter, yet the laboratory exercises were illustrations of the text proper rather than working notes for the student. A further source of confusion lay in the fact that the experiments capable of being performed by the student were hopelessly mixed with those intended for the teacher. When the separate "*laboratory manual*" appeared it was *usually* characterized by the same faults.

Within recent years many new text-books of Chemistry have been written for secondary schools, but, with a few exceptions, the new books, like the old ones, are impractical. They are either too diffuse in description, the laboratory work being left chiefly to the invention of the teacher, or they are *merely* laboratory manuals, without enough descriptive matter to make them useful as text-books. Moreover, the laboratory exercises of *many* modern books are *wholly beyond* the capabilities of the average student.

There is, therefore, a demand for a text-book of Chemistry containing an adequate and scientific account of such of the fundamental facts, laws, and theories of the subject as are adapted to the needs of secondary schools, and also *specific directions* for the laboratory work, — directions that have been *tested* and found *practicable.* This demand it is the design of the present book to meet.

The authors have had exceptional opportunities to know the capacity of the average student and the training of the average teacher of science in secondary schools. They are fully aware of the limitations of these schools both as to laboratory equipment and as to the time which may reasonably be expected for the study of Chemistry. They have prepared the book with these limitations constantly in mind.

A connected treatment of the descriptive matter of this work is attained by the division of the book into three parts: (1) the text proper; (2) the laboratory exercises; (3) the handbook. The text and the laboratory exercises are bound together; the handbook is in pamphlet form.

The **text proper** may be characterized by saying that it recognizes the fact that the terms and the ideas of Chemistry are *outside of the common experience*, and that it is useless to expect the pupil to grasp theoretical conceptions before he has become acquainted with the fundamental phenomena of the science. The arrangement of topics is such that the early chapters of the book are mainly descriptive; theoretical ideas are not introduced until later, and then only in an elementary manner.

An illustration of the arrangement is the case of molecular masses, atoms, and atomic masses, which are not mentioned at all until Chapter XVI, after the elements hydrogen, oxygen, chlorine, nitrogen, sulphur, and carbon, and their most important compounds, have been studied.

Equations, although introduced early to accustom the pupil to the fact that chemical reactions are *quantitative*, are for some time (up to page 69) written out in full rather than in symbolic form.

The idea of *equilibrium* is introduced first in connection with the study of diffusion; *later* its application is extended to chemical reactions.

The aim has been to make the text modern and scientific, yet not too difficult for secondary students.

The **laboratory exercises** are placed together *after* the text. The directions for these exercises are specific. The quantities of reagents to be employed have been carefully considered. The apparatus required is *simple* and within the reach of every school. The experiments are so arranged that they may be used in schools in which only one-hour laboratory periods are possible, as well as in those able to give two or more hours of consecutive time.

The experiments are *mainly* qualitative, as experience has shown that they must be, even with beginning *college* students. Several experiments of a quantitative nature have, however, been introduced; for these only the simplest apparatus is required.

In the earlier experiments, especially, the directions are *very explicit;* the teacher should, therefore, be able to use his laboratory time *from the beginning* in questioning individual students and in directing their work *at close range.*

Much material designed chiefly for the teacher's use has been put into the **handbook.** The handbook contains, also, a list of experiments to be performed by the teacher before the class. These experiments are *carefully planned,* and the directions for carrying them out, *accurate.* Every teacher will thus have at his command a series of demonstrations with which to supplement the laboratory exercises performed by the students.

The authors suggest that the several parts of this work be used as follows:

(1) The student is to perform the experiments for the week in the laboratory, taking notes upon his work. These notes are to be examined weekly by the teacher.

(2) The teacher is to perform the demonstration experiments for the week, the class taking notes.

(3) The teacher is to assign topics for recitation. These topics should demand (*a*) an account of the laboratory work, (*b*) a description of the teacher's experiments, (*c*) a study of assigned portions of the textbook (supplemented by other books, if possible), and (*d*) the working of certain exercises selected from those given at the end of almost every chapter.

The authors believe that if there are five one hour periods allowed for Chemistry, the best results will be obtained if *two* of these periods are given to laboratory work, *one* to the teacher's experiments, and *two* to recitation. Other plans of work may, of course, be better adapted to individual teachers.

The authors acknowledge their indebtedness to the long list of persons who have written upon elementary Chemistry in the past, and without whose work the preparation of a book like this would be almost impossible.

They wish, further, to express their thanks to Dr. Alexander Smith, of the University of Chicago, who suggested the apparatus and method of making sulphuric acid (Fig. 41); to Dr. Oliver C. Farrington, of the Field Columbian Museum, Chicago, and to Mr. Ben Hains, Crawfordsville, Ind., for the cut of Marengo Cave (Fig. 46); to Mr. A. H. Hutchinson, manager of the Ice and Refrigerating Department of the Frick Company, Waynesboro, Pa., for the cut of the ammonia apparatus (Fig. 34), and to the United Gas Improvement Company, Philadelphia, Pa., for the cut of the water-gas apparatus (Fig. 50).

To the book as published in April, 1902, there are now added a chapter on Organic Compounds and several new laboratory exercises. The Qualitative Scheme in Experiment LXXXV is that of Professor T. W. Richards (Harvard Requirements, page 20). Experiment LXXXVI was suggested by Mr. R. H. Brownlee, of the University High School.

J. C. H.
A. L. S.

CHICAGO, ILL., June, 1905.

PUBLISHER'S NOTE.

INSTRUCTORS in Chemistry need not be told that it is now the custom of lecturers on this subject to use the *arrow* interchangeably with, and more often in place of, the equality sign. This is done in this book. It makes the equation plain, and, to the chemist, means more than does the usual (old) sign of equality. Its use is fully explained on page 69. The *double arrow*, first used on page 263, shows a "reversible reaction," which cannot be represented by the usual equality signs.

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CHEMISTRY.

INTRODUCTION.

1. Definition of Chemistry. — Chemistry may be defined as the science which deals with the *different kinds of matter and their transformations.* The kinds of matter are called *substances.* Many substances occur ready-formed in the earth; but many others are not so found, and must be made from existing bodies. Chemistry, therefore, consists largely of a *description* of the ways in which substances occur in nature, of the methods by which they may be produced in the laboratory, and of the properties, or characteristics, by which they may be distinguished from one another.

Descriptive Chemistry alone, however, cannot give a connected and an intelligent view of the whole science; this can result only from a study both of the *laws* governing chemical phenomena, and of the most important *theories* that men have suggested to explain the laws.

2. Importance of Chemistry. — The ideas of modern Chemistry are of great importance, both for their own sake, and because they add so much to other departments of knowledge; no *apology* is therefore needed for the presence of Chemistry in a course of study. We may, however, summarize in brief form the reasons why every student in a secondary school should master at least the elements of chemical science: —

1. A good course of laboratory work in Chemistry disciplines the mind, as few courses can, in independent and honest observation of phenomena.

2. A knowledge of this science is necessary for the intelligent study of other natural sciences, such as geology, astronomy, biology, physiology, etc., which make *special* application of its *general* ideas.

3. Chemistry is *intensely practical*, for its facts are in the most common use in the arts and in every-day life.

As illustrations of the practical character of chemical knowledge we may cite its application in medicine, in sanitation, in domestic science, in the extraction of metals from their ores, in the refining of petroleum, and in the manufacture of steel, illuminating and fuel gas, paints, dyestuffs, food products, ice, alcohol, soap, glass, paper, explosives, etc.

To be sure, it is impossible for an *elementary* course in Chemistry to give *all* the facts relating to such topics as those suggested above; but it does give the facts and the theories that are *fundamental*, and by means of which even more complex phenomena must be interpreted.

3. Relation between Chemistry and Physics. — Chemistry and Physics are closely related sciences, for both together have as their object the study and the explanation of the *general* phenomena, or changes, that take place in the material universe. They are, in fact, two points of view from which natural phenomena may be considered. *Physics* has to do chiefly with transformations of energy, and with matter only as that upon which energy acts to produce phenomena. *Chemistry*, on the other hand, is largely concerned with the various *forms* of matter, and with energy-changes only as they result in the formation of **new substances**.

Accordingly, phenomena are usually distinguished as either *physical* or *chemical* phenomena. To the former class belong those changes in which the substance, in connection with which the energy manifests itself, is not *permanently* altered, but *regains* its original properties. A physical change may, therefore, be repeated with the same substance after the substance has resumed its former condition. Illustrations are: the magnetization of a knife-blade; the production of light by means of white-hot iron; the melting of ice, and the vaporization of water.

Chemical phenomena, on the other hand, involve a permanent alteration of the properties of the substances used. Thus, a piece of burnt magnesium does not assume its original condition on cooling; rusted iron is no longer iron; carbonic acid gas is neither carbon nor oxygen, although these two substances were put together to produce it.

In the same way we distinguish between the *properties* of substances, calling those properties *physical* which require only *physical* phenomena for their exhibition, and those properties *chemical* which are capable of being manifested only by some *chemical* change.

Thus the color, specific gravity, melting point, crystalline form, solubility, etc., of sulphur would be termed *physical* properties of sulphur; its power of burning in air is, on the contrary, a *chemical* property.

The description of a substance in Chemistry includes its most important physical, as well as its chemical, properties.

4. **Reagents and Reactions.** — Substances which have a chemical effect upon one another are said to *react*, and a chemical change is therefore called a *reaction.* The substances which react are called *reagents*, or *factors.* Thus, when copper is treated with concentrated nitric acid, a *chemical reaction* takes place, and the copper and the nitric acid are the *reagents* (or factors).

The adjective "reagent" is often applied to substances in the form in which they are commonly used in the laboratory. Thus "reagent" ammonia means an *aqueous solution* of ammonia; ammonia itself is a gas. Similarly, by "reagent" sodium hydroxide we mean the solution of solid sodium hydroxide in water, this being the form in which sodium hydroxide is most frequently used in the laboratory.

5. **Elements and Compounds.** — Almost all of the substances found in the earth may be shown, by one method or another, to consist of two or more *different* kinds of matter, and are therefore called *compound substances*, or *compounds*. There are, however, between seventy and eighty substances which it is impossible for us to decompose, *with our present methods*, into simpler kinds of matter; these substances are, therefore, called **elementary substances,** or simply **elements.**

Less than half of the substances believed to be elementary are really found *free* in the earth and its atmosphere; the others occur only in a combined form.

Although the number of elements is so small, the number of compounds they are actually known to form is very large — probably not less than one hundred thousand. The number of compounds *theoretically* possible, but not yet known to exist, is also very large.

A list of the substances usually considered elementary follows
The letter, or combination of letters, given after the name
each element is called the *symbol* of the element. It is not
tended that all these symbols shall be learned now, but rat
by association with the names of the elements as the latter ar
studied. In cases in which symbols are formed from the Latin (or Greek) names of the elements instead of the English names, both names are given.

ELEMENTS.	SYMBOLS.	ELEMENTS.	SYMBOLS.
Aluminum	Al	Neodymium.	Nd.
Antimony	Sb.	Neon.	Ne.
Argon	A.	Nickel.	Ni.
Arsenic	As.	Niobium.	Nb.
Barium	Ba.	Nitrogen.	N.
Beryllium (Glucinum).	Be. (Gl.)	Osmium.	Os.
Bismuth	Bi.	Oxygen.	O.
Boron	B.	Palladium.	Pd.
Bromine.	Br.	Phosphorus.	P.
Cadmium	Cd.	Platinum.	Pt.
Cæsium.	Cs.	Potassium (Kalium).	K.
Calcium	Ca.	Praseodymium.	Pr.
Carbon	C.	Rhodium.	Rh.
Cerium	Ce.	Rubidium.	Rb.
Chlorine.	Cl.	Ruthenium.	Ru.
Chromium.	Cr.	Samarium.	Sm.
Cobalt	Co.	Scandium.	Sc.
Copper (Cuprum).	Cu.	Selenium.	Se.
Erbium	Er.	Silicon.	Si.
Fluorine.	Fl.	Silver (Argentum).	Ag.
Gallium.	Ga.	Sodium (Natrium).	Na.
Germanium.	Ge.	Strontium.	Sr.
Gold (Aurum).	Au.	Sulphur.	S.
Helium.	He.	Tantalum.	Ta.
Hydrogen.	H.	Tellurium.	Te.
Indium.	In.	Thallium.	Tl.
Iodine.	I.	Thorium.	Th.
Iridium.	Ir.	Tin (Stannum).	Sn.
Iron (Ferrum).	Fe.	Titanium.	Ti.
Krypton.	Kr.	Tungsten (Wolframium).	W.
Lanthanum.	La.	Uranium.	Ur.
Lead (Plumbum).	Pb.	Vanadium.	Vd.
Lithium.	Li.	Ytterbium.	Yb.
Magnesium.	Mg.	Yttrium.	Y.
Manganese.	Mn.	Xenon.	Xe.
Mercury (Hydrargyrum).	Hg.	Zinc.	Zn.
Molybdenum.	Mo.	Zirconium.	Zr.

Besides the elements given in the above list, there are several other substances which are considered by some chemists to be elementary, but, the true nature of these substances being still in dispute, their names are omitted here. See pages ii and iii of Appendix.

6. Relative Abundance and Importance of the Elements. — The elements are by no means equally abundant; nor are they all of equal importance for the organic forms existing upon the earth. It is probable that only eleven are *absolutely* essential to animal life. These are, —

Carbon,
Oxygen,
Nitrogen,
Hydrogen,
Sulphur,
Calcium,
Sodium,
Chlorine,
Phosphorus,
Potassium,
Iron.

If four more were present, viz.: —

Silicon,
Aluminum,
Magnesium,
Fluorine,

savage life, upon an earth similar to ours, would be possible.

With seven additional elements, viz.: —

Gold,
Silver,
Platinum,
Tin,
Zinc,
Manganese,
Mercury,

modern civilization might exist.

The great inequality in the distribution of the elements is shown, in a rough way, by Fig. 1. As there indicated, silicon and oxygen together make up about *three fourths* of the earth's solid crust.

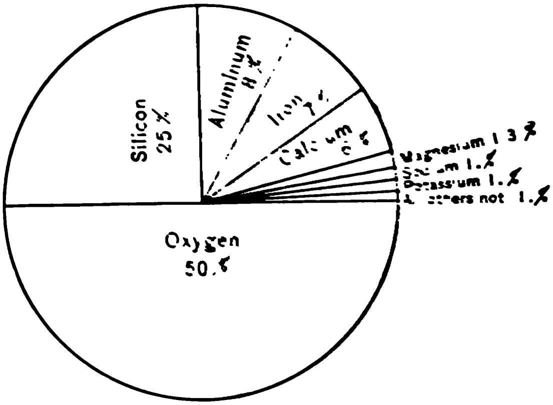

FIG. 1.

We shall begin our study of Chemistry in Chapter I with the element that is in some respects the most remarkable of all, — the element **hydrogen.**

7. Exercises.

Classify the following as either physical or chemical phenomena: —

The souring of milk, the burning of wood, the evaporating of water, the tarnishing of silver, the dissolving of sugar in water, the bleaching of muslin, the melting of lead.

CHAPTER I.

HYDROGEN.

8. Existence. — Hydrogen is a light, colorless gas that is found in a *free* condition only in comparatively small amounts on the earth — chiefly in the air and in volcanic gases. It exists in great quantities, however, in the atmosphere of the sun. Although rare in the uncombined form, hydrogen is a constituent of many important and abundant compounds, such as organic substances, water, acids, etc. The most common compound of hydrogen is water. One ninth, by weight, of water is hydrogen, and the remainder is another colorless gas, viz., oxygen.

The name "hydrogen" means "a producer of water"; while "oxygen" means "a producer of acids."

9. Common Method of Preparation. — Since water is a compound of hydrogen, the decomposition of water will, of course, give hydrogen; but a much more convenient way to prepare the gas is to decompose certain *acids*. Acids, like water, contain hydrogen, and give it up readily when treated with certain metals under appropriate conditions. The metal commonly used is zinc, and the acid either hydrochloric or dilute sulphuric acid.

Generation and Collection of Hydrogen.

The gas is usually produced in a bottle or flask (Fig. 2) provided with a "thistle" or "safety" tube and a delivery tube reaching into the water of a water pan (called also a "pneumatic trough"). The bottle contains zinc. Acid is added through the thistle tube until the lower end of the thistle tube is immersed; the evolved gas escapes through the delivery tube and bubbles up through the water in the pan. Here the hydrogen may be collected in appropriate "receivers" (test tubes, bottles, etc.) filled with water and inverted over the end of the delivery tube. Or, since hydrogen is much lighter than air, it may be collected by displacing the air of the receiver, as is shown in Fig. 3.

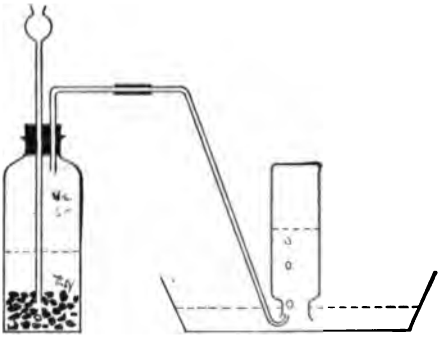

FIG. 2.

N. B. Apparatus in which hydrogen is being generated must *not* be brought *near a flame!*

If the action between metal and acid is not brisk, it may be hastened by adding a few drops of copper sulphate solution. The copper sulphate reacts with a portion of the zinc, precipitating copper, which forms a black deposit upon the zinc; thus coated, the latter acts readily upon the acid. The action of zinc and acid results in a very considerable evolution of heat.

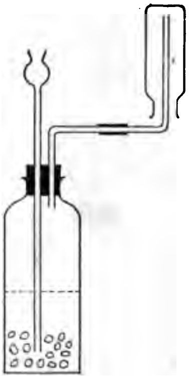

FIG. 3.

Self-Regulating Generator.

Instead of the ordinary generating flask, a Kipp's or other self-regulating apparatus may be used to supply hydrogen. Kipp's apparatus (Fig. 4) consists of three globes. The upper globe is in communication with the lower globe, and the middle globe with the lower globe, but the upper globe and the middle globe are not connected. The upper and lower globes contain dilute acid, but the middle globe contains zinc. This is the condition of the apparatus when at rest, with the stopcock closed. When the stopcock is opened, the liquid of the upper globe falls into the lower globe, and the liquid in the lower globe rises into the middle globe, thus displacing the gas of the middle globe, and forcing it out through the stopcock. The acid which enters the middle globe reacts with the zinc, forming more hydrogen, which either escapes through the stopcock, or, if the latter is closed, forces the acid back into the lower globe and thence into the upper globe. The gas in the middle globe is thus ready for instant use.

10. Purification of Hydrogen. — If the metal or the acid used in preparing hydrogen is of "commercial"

grade, the hydrogen will be *impure,* **as may be inferred from its disagreeable** odor. We may remove most of **the impurities — as** well as volatile acid, if hydrochloric acid is used — by passing the gas through a mixture of *sodium hydroxide* and *potassium permanganate* solutions. To dry it we use some *dehydrating agent,* e. g., granular calcium chloride.

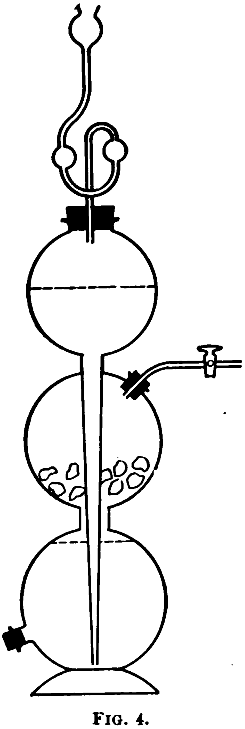

FIG. 4.

The apparatus for preparing comparatively pure hydrogen is shown in Fig. 5.

The hydrogen is generated in a flask (or Kipp's apparatus), and is passed through a bottle containing potassium permanganate dissolved in 10% sodium hydroxide solution, and then through a U-tube of calcium chloride. A second bottle of the permanganate solution will make the purification more complete. The exit tube of the U-tube is drawn out to a small opening, so that the hydrogen shall issue in a steady stream. If the washing of the hydrogen by the "alkaline permanganate" solution has been successful, the gas will now be practically odorless.

The stream of gas may be lighted if the following **precautions** are observed: —

In every case, before we light a jet of hydrogen (the same precautions apply to other inflammable gases), we collect a test tube full by displacing the air, and then carry the test tube — in this case, mouth down — to a gas jet or other flame at least *four feet* away. The gas in the test tube is thus set on fire, with explosion, if there is still much air mixed with the hydrogen, but quietly, if the air originally in the apparatus has been displaced. We then carry the test tube back to the stream of hydrogen and repeat the operation with freshly collected test tubes full of the gas, until the hydrogen stream is lighted.

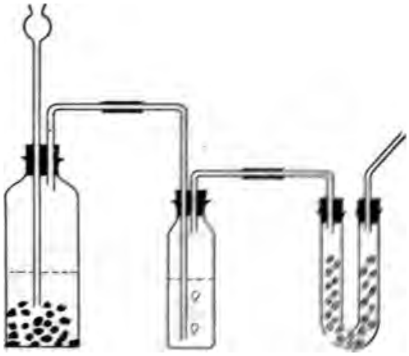

FIG. 5.

The reason for all this precaution is that it is unsafe to light a confined mixture of hydrogen and air; and we can be sure that the displacement of the air in the apparatus is complete only when the time needed for the burning of the test tube of hydrogen is greater than that required for the return of the test tube to the jet of hydrogen.

The action of [illegible] **dilute sulphuric acid gives,**

besides hydrogen, a substance called **zinc sulphate.** This remains in the solution, but may be **obtained from** it as a white, crystalline solid.

11. Chemical Properties. — The hydrogen flame is almost colorless, but very hot, as holding a piece of platinum in it will show. Indeed, there is enough heat liberated by the burning of a gram of hydrogen in oxygen gas to raise the temperature of about 34,000 grams of water 1° C., or about 340 grams from the freezing point to the boiling point.

An apparatus for making use of this great heat evolution is *the oxyhydrogen blowpipe* (Fig. 6). This consists of a small inner tube communicating with a tank of oxygen, and a larger outer tube in connection with a tank of hydrogen. Both gases are greatly compressed. The hydrogen is first turned on and lighted; then the oxygen is allowed to escape *very slowly*. Thus a flame is produced which is so hot that it will melt platinum. (Platinum melts at about 1700° C.) A piece of quicklime held in the oxyhydrogen flame becomes white hot and gives off much light; this is the so-called *calcium*, or *lime*, light. In the production of the lime light for stereopticons, illuminating gas is generally used instead of hydrogen. The ordinary blast-lamp of laboratories is similar to the oxyhydrogen blowpipe, but the gases used are illuminating gas and ordinary air; as a result, the temperature produced is by no means as high as that of the oxyhydrogen flame.

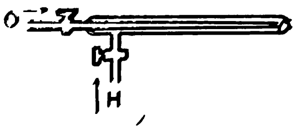

FIG. 6.

The hydrogen flame has *only one zone*, or region, *of* *combustion.* A vertical section of it would have the appearance shown in Fig. 7, —

a is the central space of unburned hydrogen;
b is the region of combustion.

The bearing of this fact will be understood when we come to study more complex flames.

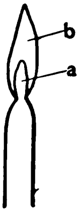

FIG. 7.

12. Union of Hydrogen with Oxygen. — *The product formed when hydrogen burns* in air is **water,** as we may prove readily by holding over the burning hydrogen a beaker of cold water (Fig. 8). Although the beaker was dry on the *outside* at the beginning of the experiment, it will soon condense drops of water from the flame. The water may be easily collected and identified.

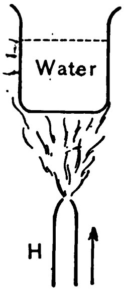

FIG. 8.

In burning, hydrogen takes **oxygen** from the air; in fact, *every case of combustion in air consists in the union of the substance burned with the oxygen of the air.* Hydrogen does not, however, *support* combustion; that is to say, burning wood, paper, illuminating gas, etc., — the ordinary combustibles, — do not continue to burn when placed in an atmosphere of hydrogen.

Hydrogen is really *inert* at ordinary temperatures, and active only when the temperature is raised considerably. This is shown by the fact that even hydrogen and oxygen may be mixed and kept together for an indefinite period without evidence of action. The inertness of hydrogen under ordinary conditions is such that it is often convenient to experiment with a substance in an atmosphere of this gas, thus excluding the active oxygen of the air.

At about 650° C., however, hydrogen and oxygen unite with great violence. Although only a very small amount of the mixture of the gases is really heated to 650° C. by the match or electric spark used to start the combustion, yet the burning of this portion causes so much heat to be given off that adjacent portions are quickly raised to the required temperature; as a result, union takes place very rapidly through the whole mixture. The explosion seems instantaneous, but is not; its rate has been determined by photography to be a little less than *two miles a second.*

If the union of oxygen and hydrogen takes place at a pressure lower than the ordinary atmospheric pressure, the rate of the explosion and, consequently, its violence, is much diminished.

Hydrogen has the power of combining not only with *free* oxygen, but also, in many cases, with oxygen that is in combination with other elements. Thus, if hydrogen is passed over heated copper oxide and lead oxide, it unites with the oxygen of these substances, forming water, and setting free copper and lead, respectively. These are illustrations of the *reducing*, i. e., *deoxidizing*, power of hydrogen.

13. Occlusion of Hydrogen. — A remarkable property of hydrogen is its absorption in large quantities by certain metals, *e. g.*, platinum and palladium. The hydrogen is said to be "**occluded**" by these metals. The phenomenon may be illustrated by holding a piece of platinum sponge in a jet of dry hydrogen; so much heat is evolved during the occlusion of the hydrogen that the latter is set on fire.

The ready union of hydrogen and other inflammable gases with air, in the presence of platinum, may be shown by directing the mixture of cold gases issuing from a Bunsen burner against a piece of hot platinum foil. The gases will unite with so great an evolution of heat that the platinum will continue to glow.

Palladium has an even greater power of occluding hydrogen than platinum has. One volume of palladium can absorb about *375* volumes of hydrogen at the ordinary temperature!

14. **Physical Properties.** — As we have already learned, hydrogen is a colorless and odorless gas. It is the lightest substance known, air being about 14.4 and oxygen about 16 times as heavy (*cf.* Appendix iv). The weight of one liter of hydrogen at 0° C. and 760 mm. pressure is about .09 gram; there are, therefore, no less than *11 liters of the gas to the gram.*

Hydrogen is the standard of density in the case of gases; its relative density is 1.

The rate at which hydrogen *diffuses*, i.e., mixes with other gases, is four times that of oxygen. A special form of diffusion, viz., *transpiration*, may be illustrated as follows: —

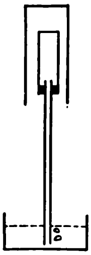

FIG. 9.

A porous cup (Fig. 9) is attached securely to a glass tube ending under water. If, now, a bell-jar or a large bottle filled with hydrogen is placed over, and enclosing, the porous cup, bubbles of gas will be seen escaping from the lower end of the tube.

The explanation of the phenomenon is that the two gaseous media, air and hydrogen, separated by the porous partition, tend to form a homogeneous mixture. But the rate at which the hydrogen passes through the partition is so much greater than that of the air, that an increase of volume, and, therefore, of pressure, occurs within the porous cup. Consequently some of the gaseous mixture escapes. When the bell-jar is removed, the *reverse* diffusion takes place.

A somewhat simpler form of apparatus is shown in Fig. 10. A wide glass tube has one end covered with a cap of plaster of Paris. If the tube is filled with hydrogen by displacing the air, and the open end is placed *at once* under water, water will rise in the tube.

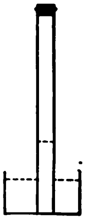

FIG. 10.

Hydrogen is not very soluble in water; at 14° C. 100 c.c. of water absorb only 1.9 c.c. of the gas.

At the ordinary temperature, hydrogen cannot be liquefied by any pressure, however great; but by intense cold, in addition to great pressure, the gas has been condensed to the liquid and solid state. Liquid hydrogen is a colorless substance less than one tenth as heavy as water. It boils at about —240° C., at the ordinary pressure.

Hydrogen is a better conductor of heat and of electricity than any other gas.

15. Other Methods of Preparation. — The action of metals upon acids is only one of many methods by which hydrogen may be prepared; other general methods are the following: —

(*a*) The decomposition of water by the electric current. This operation is called the "electrolysis" of water; it takes place only when the water contains small quantities of certain substances called "**electrolytes.**" The electrolyte commonly used is dilute sulphuric acid.

(*b*) The action of certain substances — chiefly metals — upon water. Some metals, *e. g.*, sodium and potassium, act violently even upon *cold* water; others, like magnesium, zinc, and iron, decompose only *hot* water, or steam.

(*c*) The action of metals upon basic hydroxides, *e. g.*, aluminum filings upon sodium hydroxide solution.

16. Quantitative Character of Chemical Changes. — When hydrogen unites with oxygen to form water, the relation between the masses of the elements entering into combination is a definite and constant one.

Eight parts, by weight, of oxygen combine with one part of hydrogen.

The relation between the mass of hydrogen burned and that of the water formed is also constant; one part of hydrogen always forms by its combustion *nine* parts of water.

Conversely, *nine* parts by weight of water give, when decomposed, *eight* parts of oxygen and *one* part of hydrogen.

Similarly, an exact relation exists between the masses of zinc and sulphuric acid which react with each other, and between each of these and the masses of hydrogen and of zinc sulphate formed. This relation is as follows: —

Sixty-five parts by weight (grams, pounds, etc.) of zinc and 98 parts of sulphuric acid (diluted with water) give 161 parts of zinc sulphate and two parts of hydrogen.

It may be proved by the most careful weighing that *when zinc reacts with sulphuric acid there is no gain or loss of matter*, but only the liberation of 2 grams of hydrogen by every 65 of zinc. If the quantities of zinc and sulphuric acid taken are in exactly the correct proportion, and the resulting solution is evaporated, neither zinc nor sulphuric acid will remain; and the zinc sulphate obtained will contain all the matter of the zinc and of the acid used except the hydrogen, which escaped from the solution.

17. Calculation of Quantities of Factors and Products. — Since the reaction between zinc and sulphuric acid takes place in definite proportions by weight, it is always possible for us to calculate how much acid will be required to react exactly with a given mass of zinc, and how much hydrogen and zinc sulphate will be formed.

Suppose, for example, that we wish to know *how much sulphuric acid is needed to react exactly with 40 grams of zinc.*

Since 65 grams of zinc require 98 grams of sulphuric acid for complete action, 40 grams of zinc will require a proportional amount of the acid. The amount needed may, therefore, be determined by solving the proportion, —

$$65 : 40 : : 98 : x$$

$$\text{whence } x = 60.3 \text{ grams.}$$

This is, of course, the *least* quantity of sulphuric acid that will use up all of the zinc. If a larger amount is used, the excess will simply remain in the solution.

If we wish to find the amount of zinc needed to produce 5 grams of hydrogen, we may do so by solving for x in the proportion, —

$$65 : x : : 2 : 5$$

$$\text{whence } x = 162.5 \text{ grams.}$$

To find the volume at 0° C. and 760 mm. pressure of the 5 grams of hydrogen produced, we divide the number of grams of hydrogen by the weight, in grams, of one liter of hydrogen at 0° C. and 760 mm. pressure; *i. e.*, by 0.09.

The volume of the 5 grams of hydrogen is thus, —

$$55.5 + \left(= \frac{5}{.09}\right) \textit{ liters.}$$

If we *reverse* the conditions of the problem, and ask how much zinc is required to produce by its action with sulphuric acid 40 liters of hydrogen at 0° C. and 760 mm. pressure, we must first find the *weight* of the 40 liters of hydrogen at 0° C. and 760 mm. pressure, and then calculate the weight of zinc necessary.

The weight of 40 liters of hydrogen under the given conditions is 3.6 (= 40 × 0.09) grams; the weight of zinc needed is then calculated from the proportion, —

$$65 : x :: 2 : 3.6.$$

When zinc reacts with hydrochloric acid the products are *zinc chloride* and *hydrogen*. The relative quantities are as follows: —

65 grams of zinc and 73 grams of hydrochloric acid give 136 grams of zinc chloride and 2 grams of hydrogen.

18. Exercises.

1. Learn or review the metric tables of weight, of length, and of volume.

2. How many cubic centimeters in 1 liter? In 1 c. dm.? What is the relation between g., mg., dg., cg., kg.? What is the weight of 106 c.c. water? State the relation between 1 mm., 1 cm., 1m., and 1 dm.

3. How many grams of hydrogen can be stored in a 36-liter gasometer under conditions at which 1 liter of hydrogen weighs .09 grams?

4. What properties of hydrogen make it useful as the inflating gas of balloons? What properties make it disadvantageous?

5. How many grams hydrogen can be obtained by the

action of 20 grams zinc upon an excess of dilute sulphuric acid? Upon an excess of hydrochloric acid?

6. What is the volume in cubic centimeters of 30 grams water? Of 30 grams platinum of S.G. 21.5? Of 30 grams ether of S.G. 0.72?

quantity of material taken and that of each of the products formed is *definite* and *constant*.

Thus, 122.5 grams of potassium chlorate give 48 grams of oxygen and 74.5 grams potassium chloride.

The ease with which potassium chlorate decomposes in the presence of manganese dioxide was unexplained for a long time; but it is probably due to the fact that the two substances react to form intermediate compounds, which are decomposed again. The heating of a mixture of manganese dioxide and potassium chlorate to about 200° to 250° C. thus results in the decomposition of the *potassium chlorate*, while it leaves the manganese dioxide unchanged.

21. Other Methods of Preparing Oxygen. — Three other methods of preparing oxygen will be described briefly; these are, —

(1) Decomposition of mercuric oxide.
(2) Decomposition of barium peroxide.
(3) Decomposition of manganese dioxide.

The *first* method is the historic one of **Priestley,** who discovered oxygen in 1774, and of **Scheele** (pronounced Shālā), who discovered it independently in 1775.

When mercury is heated in air to a temperature a little below the boiling point of the mercury (mercury boils at 357° C.), it unites with a definite weight of oxygen to form *mercuric oxide*, or *red oxide of mercury*.

25 parts by weight of mercury and 2 parts of oxygen give 27 parts of mercuric oxide.

Mercuric oxide is a stable compound at ordinary temperatures; but when it is heated to a temperature a little higher than that at which it was formed, it is decomposed again into mercury and oxygen.

27 grams of mercuric oxide always yield 25 grams of mercury and 2 grams of oxygen.

Barium peroxide, the second substance named above as a source of oxygen, is a white solid which gives up half of its oxygen when heated; the other half remains in combination with the barium in the compound *barium monoxide.* Under appropriate conditions barium monoxide takes up from the air as much oxygen as it already holds, and thus forms the *peroxide.* Apparatus has been devised in which these changes take place alternately, and large quantities of oxygen are thus produced for sale.

169 grams of barium peroxide give 153 grams of barium monoxide and 16 grams of oxygen.

It is evident that the oxygen formed in both the first and the second methods is taken from the air.

Manganese dioxide, the third substance named above, is called, also, "*black oxide of manganese.*" It is found in nature as the mineral **pyrolusite.** Manganese dioxide decomposes at about 600° C., giving off a *third* of its oxygen.

261 grams of manganese dioxide give 229 grams of manganous-manganic oxide and 32 grams of oxygen.

22. Physical Properties of Oxygen. — In whatever way it is prepared, oxygen is colorless, odorless, and tasteless, if pure. It is somewhat heavier than air, and sixteen times as heavy as hydrogen. One liter of oxygen at 0° C. and 760 mm. pressure, weighs 1.43 grams.

Gaseous oxygen may be condensed at —118° C. and 50 *atmospheres* (= 50 × 760 mm.) pressure, to a bright blue liquid.

Oxygen is more than twice as soluble in water as hydrogen; 100 c.c. of water dissolve about 4 c.c. oxygen under ordinary conditions.

Oxygen is the most abundant element, composing about half of the earth's *solid* crust, eight-ninths of the water, and 23% by weight of the atmosphere. It is an essential constituent of all living things.

23. Chemical Properties. — The chief chemical property of oxygen is its energetic support of combustion; for substances that burn in air burn much more rapidly in oxygen. Thus, a pine splinter which is merely glowing in the air will burst into flame if put into oxygen. Combustion in air is more slow than in oxygen, because the oxygen of the air is diluted with almost four times its volume (= more than three times its weight) of inert gases which do not support ordinary burning at all.

Examples of substances which burn readily in oxygen are: Iron, which burns with *scintillation*, forming the magnetic oxide of iron; magnesium, phosphorus, and sulphur, which burn with intensely brilliant *flames*; and charcoal, which burns with a *glow*, as in air, but much more brightly. These substances unite with oxygen in the following proportions: —

21 grams of iron and 8 grams of oxygen give 29 grams of magnetic iron oxide.

3 grams of magnesium and 2 grams of oxygen give 5 grams of magnesium oxide.

31 grams of phosphorus and 40 grams of oxygen give 71 grams of phosphorus pentoxide.

1 gram of sulphur and 1 gram of oxygen give 2 grams of sulphur dioxide.

3 grams of carbon (charcoal) and 8 grams of oxygen give 11 grams of carbon dioxide.

The magnetic oxide of iron is a black solid; magnesium oxide and phosphorus pentoxide are white solids — the latter is very soluble in water; sulphur dioxide and carbon dioxide are colorless gases. Sulphur dioxide has the characteristic odor of burning sulphur.

24. Oxides. — Because of the readiness with which oxygen unites with other elements, the most common compounds in which elementary bodies are found are **oxides.** Fluorine and the argon family alone, of all the elements, form no oxygen compounds so far as known.

Many oxides may be made directly from the elements, *e. g.*, water, and copper oxide; but many must be made *indirectly*, *e. g.*, platinum oxide. To obtain the latter substance the metal platinum must first be converted into other compounds, and these into the oxide. Nitrogen, too, although incombustible in the ordinary sense, yet forms, by indirect methods, five different oxides.

25. Oxidation and Reduction. — To the union of oxygen with other substances we give the name **oxidation,** and to a substance which gives up some of its oxygen to another body the name **oxidizing agent.** Of course the oxidizing agent is itself *reduced,* i. e., loses oxygen, when it oxidizes another substance — there can be no *oxidation* without a corresponding *reduction.* The substances mentioned in this chapter as sources of oxygen are all *oxidizing agents:* carbon and hydrogen (*cf.* § 12) are common examples of reducing agents.

26. Deflagration. — When a solid or liquid combustible substance is mixed with a solid or liquid oxidizing agent, and the temperature is raised sufficiently, the combustion does not proceed from one part of the combustible to another, as is the case when the combustible burns in air: on the contrary, union takes place almost instantaneously through the *whole* mixture, just as it does through a mixture of gaseous hydrogen and oxygen. This rapid union of combustible and oxidizing agent is called **deflagration.**

A common case of deflagration is that of gunpowder, which is a mixture of charcoal and sulphur (reducing agents) with potassium nitrate, or potassium chlorate (oxidizing agents). When ignited in air, gunpowder *deflagrates.* In an enclosed space the same action takes place, but the gaseous products of the combustion are held for an instant under great pressure. When this pressure is released, the expanding gases are capable of hurling a projectile, or of tearing apart masses of rock.

27. Combustion. — When a substance unites directly with gaseous oxygen we speak of the oxidation as a case of *burning*, or *combustion.* Of this we generally distinguish two kinds, (1) *ordinary* and (2) *slow* combustion.

In *ordinary* combustion, heat is produced by the union of combustible with oxygen much more rapidly than it can be dispersed by conduction, radiation, etc.; consequently the temperature of the burning body rises far above that of the surrounding medium. Usually a part of the combustible, or of the products of combustion, becomes *incandescent ;* and some of the energy liberated appears in the form of light.

28. Slow Combustion. — A *slow* combustion occurs when oxidation takes place through a long period of time, and, therefore, without a decided rise of temperature. This can occur only when the heat is dispersed as rapidly as it is evolved.

Decay, e.g., of wood, is a form of slow combustion ; so is the rusting of iron.

The temperature of the bodies of animals is kept up by the slow oxidations taking place within them.

Although there is a great difference in temperature between a body oxidizing slowly and one burning in the ordinary way, yet the amount of energy actually evolved by the oxidation of a given weight of a substance is the same in the one case as in the other.

Thus, a piece of magnesium oxidizes *slowly* in moist air, at the ordinary temperature, to form a white powder containing magnesium oxide and water; but we have every reason to believe that the quantity of energy set free during this slow formation of magnesium oxide is just as great as that evolved when an equal mass of the metal magnesium burns brightly in the air. That there is no perceptible heat and light in the former case is due to the fact that the evolution of heat is equaled by its dispersion.

29. Spontaneous Combustion. — When the *evolution* of heat is only a little in excess of its *dispersion*, the combustion is *apparently* a slow one; after a while, however, enough heat accumulates to set the body on fire. Slow oxidation explains so-called "spontaneous" combustions, by which heaps of oily rags, etc., ignite without apparent cause.

Spontaneous combustion may be illustrated by means of a solution of phosphorus (only a small amount must be used) in carbon disulphide. If this solution is poured upon a filter paper supported on a ring stand, the phosphorus will soon take fire "spontaneously." The explanation of the phenomenon is that the evaporation of the carbon disulphide leaves the phosphorus in the pores of the paper, where it oxidizes; and the heat generated, being prevented from escaping by the non-conducting filter paper, soon raises the temperature of some part of the paper to the ignition temperature of the phosphorus.

30. Ignition Temperature. — In all ordinary combustion there is a definite temperature, called the *ignition temperature*, or the *kindling temperature*, to which the combustible substance must be heated in order that it may begin to unite with the gas supporting the combustion. The burning substance must not only be heated *up to* the kindling temperature, but it must be kept *at least as high* as this temperature, or combustion will cease.

The ignition temperature is different for different substances. Thus, ordinary phosphorus bursts into flame, in air, at about 40° C.; while for sulphur the kindling temperature is about 260° C. In some cases the temperature of ignition is far below the ordinary temperature.

The heat evolved by the burning of one part of a substance serves to raise other parts to the ignition point; illustrations of this are found in the burning of wood, paper, etc. In the ordinary match the ignition temperature of the material composing the head is reached by friction; and the heat generated by the combustion of the head serves to raise the wood of the match to its ignition temperature.

31. Combustion in Air; Drafts. — The heat given off in combustion is taken up, not only by new portions of the burning body, but also by fresh portions of the surrounding gaseous medium; if, therefore, the latter is diluted, some of the heat available will be used in raising the temperature of the diluting gas, as well as that of the gas taking part in the combustion. Hence, in the air, which is a mixture of oxygen and nitrogen (chiefly), combustion is much slower than in pure oxygen, since the nitrogen, although it takes no part in the combustion, yet takes up much of the heat evolved by the combustion.

Moreover, when the *products* of the combustion are gaseous, they dilute the oxygen still further. Thus, when charcoal burns in an enclosed portion of air, combustion ceases long before all the oxygen is exhausted, for the reason that the carbon dioxide gas which is formed dilutes the oxygen.

If the products of the combustion are removed as rapidly as formed, the combustion will be much more nearly complete. Thus, when phosphorus burns in an enclosed portion of air over water, the product of the combustion — phosphorus pentoxide — dissolves in the water, and does not dilute the oxygen; as a result the oxygen is practically all taken up by the phosphorus. For the same reason the combustion of charcoal in an enclosed portion of air may be made much more nearly complete if carried out over sodium hydroxide solution.

The removal of the products of combustion from the "sphere of action" is accomplished in ordinary burning by means of drafts, which also bring fresh supplies of air. A *moderate* draft is thus beneficial to combustion. The air current may, however, have such a velocity that the heat evolved in the combustion is not sufficient to raise the temperature of the air supplied and of fresh portions of the burning body to the kindling temperature. Hence combustion ceases. A flame may thus be "*blown out*" by a strong current of air.

32. The Safety Lamp. — The lowering of the temperature of a flame below the kindling temperature is admirably illustrated in the safety lamp devised by Sir Humphry Davy. The lamp consists of an ordinary lantern entirely surrounded by wire gauze. When such a lamp (Fig. 12) is carried into an explosive mixture of gases, *e. g.*, hydrogen and air, the gases diffuse through the wire gauze and burn *inside* the lamp; but the heat generated is conducted away by the wire gauze instead of being communicated to the explosive mixture outside; hence an explosion of the gases *outside* of the lamp is avoided.

Safety lamps are used to prevent the explosion of the "fire-damp," — a mixture of marsh gas and air, — which often occurs in mines.

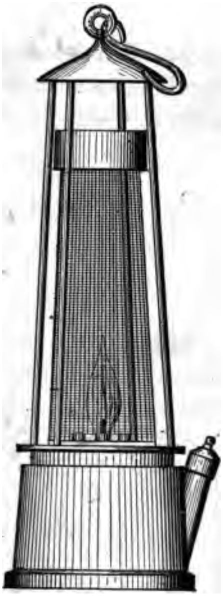

FIG. 12.

33. Flames. — *A flame is a gas in combustion.* To burn with a flame, a substance must either be gaseous itself, or it must evolve gaseous products. Such substances as magnesium, sulphur, phosphorus, and wax burn with flame because they are first converted into the gaseous form; wood and soft coal, because they evolve combustible gaseous products; but charcoal, which contains practically no volatile constituents, merely *glows*. The structure of flames will be taken up later.

34. Reversed Combustion. — We have spoken of combustion heretofore as the union of the burning body with oxygen; *other gases*, however, *may be supporters of combustion just as truly as oxygen.*

Thus, a jet of burning hydrogen continues to burn in bromine vapor; and phosphorus burns in chlorine much as in oxygen.

If both the combustible and the supporter of its combustion are gaseous, the combustion may be *reversed.* Thus, oxygen may become the burning body and illuminating gas the supporter of combustion. This reversal may be shown by a very simple experiment.

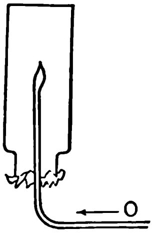

Fig. 13.

A bottle (Fig. 13) is supported, mouth downward, and filled with illuminating gas by displacing the air. The gas at the mouth of the bottle is then lighted, and while it is burning a jet of oxygen is brought up into the bottle. The oxygen takes fire at the bottle's mouth and burns in the atmosphere of illuminating gas. The oxygen jet of the preceding experiment may be replaced by a deflagrating spoon of potassium chlorate which has been heated so that it gives off oxygen.

35. Exercises.

1. How many grams of mercury will be formed by the decomposition of 43.2 grams of mercuric oxide? How many grams of oxygen?

2. How many grams of the magnetic oxide of iron will be formed when 50 grams of iron burn in oxygen?

3. How many grams of manganese dioxide are needed to give, when decomposed by heat, 12 grams of oxygen? How much manganous-manganic oxide is formed at the same time?

4. How much magnesium is contained in 30 grams of magnesium oxide? What per cent of magnesium oxide is magnesium? Oxygen?

5. Calculate the per cent of oxygen in phosphorus pentoxide.

6. How many c.c. of oxygen can be made from 1.2 grams of potassium chlorate when 1 c.c. of the gas weighs 0.0014 grams?

7. How many grams of potassium chlorate must be decomposed to fill a 36-liter gasometer (a vessel for storing gases) with oxygen at a temperature and a pressure at which 1 liter of oxygen weighs 1.25 grams?

8. What is the weight of the carbon dioxide formed by the combustion of 10 grams of carbon in oxygen? What will be the volume of the carbon dioxide under conditions at which one liter of the gas weighs 2 grams?

CHAPTER III.

WATER.

36. Nature of Water. — The union of the elements composing water is so strong that water itself was believed to be an element until 1781. In that year, Cavendish, who had discovered hydrogen in 1766, succeeded in *synthesizing* (= putting together) water from hydrogen and oxygen, and thus proved its compound nature.

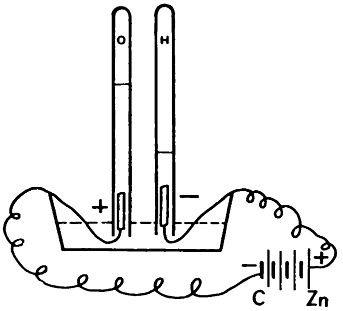

Fig. 14.

37. Electrolysis of Water. — The fact that water is a compound is proved *analytically* by its decomposition by the electric current. The operation is carried out as follows: —

A current from an electric battery (Fig. 14) — that from four Grénet cells *in series* is adequate — is passed between platinum electrodes through water containing about five per cent of its weight of sulphuric acid. While the current is passing, bubbles of gas gather upon the electrodes, and rise from them through the liquid. The gases may be collected separately by inverting over each electrode a tube filled with the dilute acid. The rates at which the two gases from the electrodes collect in the tubes is not the same; one of them — that at the negative (—) electrode — collects a little more than twice as rapidly as the other. This electro-positive (+) gas is *hydrogen;* that at the positive electrode is *oxygen.*

The relation between the volume of the hydrogen and that of the oxygen is much more nearly 2 : 1 than is usually shown by this experiment. That the ratio is generally too large is due to several slight errors, one of which is that the oxygen is much more soluble in the dilute acid than the hydrogen This error may be avoided if the gases are not collected until the liquid has become saturated with them.

The electrolysis of dilute sulphuric acid is not a direct decomposition of water by the electric current; for *pure* water is scarcely, if at all, electrolyzed in the absence of sulphuric acid, or some similar substance. It is the water, however, that is actually used up; hence we speak of the result as an electrolysis of water. The function of the sulphuric acid will be discussed later.

38. Synthesis of Water, by Volume. — The electrolysis of water gives two volumes of hydrogen for every volume of oxygen; but the *complete* proof that this is the proportion in which these gases are united in water follows from the *volumetric synthesis* of water. Thus an additional fact may be learned, viz., that the relation between the volume of the water (steam) produced and the volume of the oxygen and hydrogen taken is a *simple* one.

The apparatus required to demonstrate the volumetric synthesis of water is shown in Fig. 15.

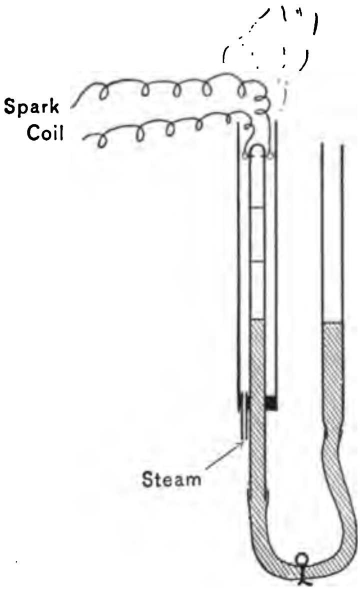

FIG. 15.

A graduated tube closed at one end has two platinum wires passing through the walls and almost meeting at the closed end. This tube — it is called a "eudiometer" tube — is filled with mercury, and its open end is placed under mercury. Part of the mercury in the eudiometer is then displaced by a mixture of pure hydrogen and oxygen put together in the proportions in which they are obtained by electrolysis. The apparatus shown in Fig. 16 is very convenient for preparing the oxyhydrogen mixture. The eudiometer is now attached securely to a rubber tube containing mercury, and is thus put into communication with a leveling tube partly full of the same metal. By raising or lowering the leveler the experimenter can compress or expand the gas in the eudiometer. He can thus get the volume of the gas at atmospheric pressure by bringing the surface of the mercury in the eudiometer and that in the leveler into the same horizontal plane. When the connections between the eudiometer and the leveler have been made, a jacket is placed about the eudiometer, the platinum wires are connected with a Ruhmkorff coil, and steam is passed through the jacket until the volume of the gas in the eudiometer becomes constant. This volume is read accurately at atmospheric pressure. The leveler is then lowered, so as to put the gas under diminished pressure; the spark is passed through the mixture; and union is effected. With the steam still running through the jacket, the mercury level in the eudiometer and in the leveler is made the same; and the volume of gas in the tube is read.

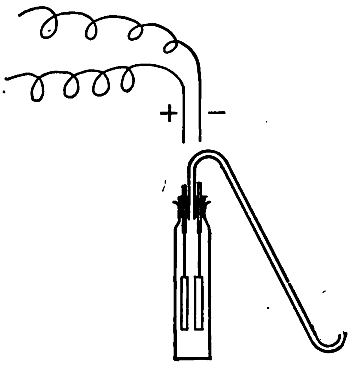

FIG. 16.

The gaseous substance in the tube after the explosion is **steam**; and *its volume is* only *two thirds as great as that of the original gases;* we have thus proved that *two volumes of hydrogen and one of oxygen unite to produce two of steam.*

This experiment has been performed many times and with great care,—the first time by Humboldt and Gay-Lussac in 1805,—and proves conclusively that the proportion by volume in which hydrogen and oxygen combine to *form* water is the same as that in which these gases are obtained *from* water.

If the apparatus for effecting the volumetric synthesis of water is used without the steam jacket, the proportions of the combining gases may be determined, but not the volume of steam produced. The volume of *liquid* water produced by the condensation of the steam is, of course, very small.

39. Synthesis of Water, by Weight. — A knowledge of the exact proportions, by weight, in which hydrogen and oxygen are combined in water is of such importance to Chemistry that many methods have been devised for the determination of the ratio. The methods are, in general, of two classes.

In methods of the *first* class a known weight of hydrogen is passed over some oxidizing agent, *e. g.*, cupric oxide; the hydrogen is thus converted into water, which is collected and weighed. The gain in weight is, evidently, *oxygen.*

In methods of the *second* class a known weight of the oxidizing agent is reduced in a stream of hydrogen, and the weight of the water formed is determined. Here the loss in weight of the oxidizing agent is plainly equal to the weight of the oxygen which united with the hydrogen; for *the water formed contains the oxygen lost* by the oxidizing agent.

The apparatus for one method of the second class is shown in Fig. 17.

Hydrogen, purified and dried by alkaline permanganate solution (B) and calcium chloride (C) respectively, is passed over heated copper oxide contained in a porcelain boat (D), and the water produced is collected in a U-tube of calcium chloride (E). A guard tube of calcium chloride (F) excludes the water of the air.

The cupric oxide is weighed before and after the experiment; its *loss* in weight is **oxygen.** The calcium chloride tube, too, is weighed before and after the experiment; its *gain* in weight represents **water.**

Berzelius and Dulong carried out this experiment, in 1819, with the following results: —

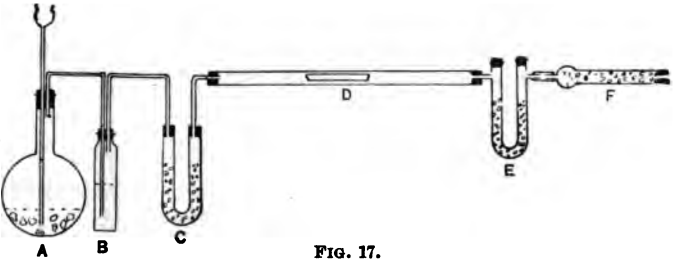

FIG. 17.

Weight of water taken up by calcium chloride $= 30.519$ g.
Loss in weight of the cupric oxide (= oxygen) $= 27.129$ g.

Therefore, weight of hydrogen united with 27.129 g. oxygen $= 3.390$ g.

$27.129 : 3.39 :: x : 1$; whence $x = 8.002 +$, the ratio of oxygen to hydrogen in water.

40. Natural Water and Its Impurities. — The water that falls upon the earth's land surface gets back to the sea in various ways, but rarely without leaching out soluble substances from the soil. *Natural water therefore contains more or less impurity.* The character of the impurity depends, (1) upon the substances present in the air through which the water fell to the earth; (2) upon the soil through or over which the water has flowed; and, also, (3) upon the opportunities the water has had of losing material previously gathered. Even rain water is far from pure, for it gathers much dust, both organic and inorganic, and many gaseous impurities of the air, e. g., *ammonia.*

Water which penetrates the earth's surface usually finds soluble substances, both solid and gaseous. The most common *soluble* solids found in water are, probably, *common salt*, *magnesium chloride*, and *gypsum;* of the gases, *carbon dioxide* and *hydrogen sulphide.* Water charged with carbon dioxide has the power to dissolve *limestone;* hence this substance is a common ingredient of natural water, even of moderately "soft" water, as is proved by the incrustations of limestone in vessels in which such water is habitually heated.

Water charged with hydrogen sulphide is called *sulphur water.*

The water which flows *over* the earth as rivers gathers its peculiar *organic* impurities from the land. These may consist of *micro-organisms* washed down by surface water, or, in the case of rivers passing large cities, of *sewage.* If the river is sluggish, these impurities are not easily removed;

but if it has a rapid current, and especially if there are rapids and waterfalls in its course, the river soon purifies itself *by bringing its impurities into contact with the oxygen of the air*, which destroys them.

41. Sea Water. — Since the sea is the ultimate destination of most of the water that falls upon the land, it is evident that the material dissolved by fresh water will accumulate in the ocean. Indeed, about four per cent *of sea water consists of dissolved material*, three-fourths of which is *common salt*. It is probable that greater or smaller amounts of all the substances composing the crust of the earth may be found in the sea.

42. The Purification of Water. — Water may usually be purified by *filtration* or by *distillation*.

Filtration serves not only to remove insoluble substances, but also to oxidize many organic impurities by bringing them into intimate contact with air.

When water is raised to the boiling temperature, most of the micro-organisms contained in the water are killed, and at least one of its inorganic impurities, viz., calcium carbonate (limestone), is rendered insoluble. *Soluble* impurities, however, still remain. To get water free from these it must be distilled.

Distillation consists in converting a liquid into vapor, and then condensing the vapor to the liquid state. When water is distilled, all impurities more volatile than the water will appear in the first portions of the distillate; all much less volatile will remain behind in the retort.

The usual form of distilling apparatus used in laboratories is shown in Fig. 18.

The condenser in the figure is called a **Liebig's condenser.** It consists of an inner tube through which the evolved vapor is passed for condensation, and of an outer jacket through which a stream of cold water is kept running in the direction shown by the arrows.

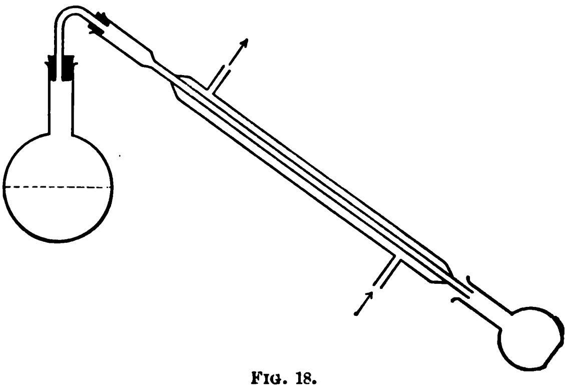

FIG. 18.

Although water can be obtained *reasonably* pure by distillation, *chemically pure* water is very difficult to prepare. Even if water is pure when freshly distilled, as shown by its leaving no residue when evaporated in a platinum dish, it cannot be kept pure long, owing to its tendency to act upon the glass or porcelain vessels in which it is stored or used.

Distilled water is "flat" to the taste. This is due largely to the fact that distilled water has lost the gases present in natural water. Distilled water may therefore be made much more palatable by shaking it thoroughly with air.

43. **Hard and Soft Water.** — Water which contains much *gypsum*, *limestone*, or similar substances in solution does not *wet* the skin readily, and is therefore called "hard" water. When soap is put into such water it does not dissolve readily, but forms an insoluble scum. It is only after the separation of this scum that soap will dissolve in quantity and form permanent suds. As will be explained later, *the hardness of water containing only limestone is temporary* because it may be removed by boiling; if gypsum is present, however, the water is *permanently* hard and can be "softened" only by the use of washing powders, etc., which are capable of converting the gypsum into insoluble forms.

44. **Properties of Water.** — Pure water is practically odorless and tasteless. In small quantities it has no color, but in large masses it is blue.

The **specific heat** of water is high, more heat being required to raise the temperature of a given weight of water one degree than is required in the case of any other substance except hydrogen.

The **latent heat** both of water and of steam is very great. When a given weight of water at 0° C. is frozen to ice at 0° C., it gives off enough heat to raise the temperature of an equal weight of water from 0° C. to 80° C. When a given weight of steam at 100° C. condenses to water at 100° C., the heat evolved is sufficient to raise the temperature of about 5.37 times the weight of water from 0° C. to 100° C.

The **boiling point of water** is 100° C. at 760 mm. pressure. Since the boiling point of a substance is the temperature at which the pressure of its vapor *just exceeds* that of the atmosphere, the "vapor tension" of water at 100° C. must be 760 mm. At 21 mm. pressure, water boils at 23° C.; at 3,581 mm., at 150° C.

The **freezing point of water** (= melting point of ice) is 0° C. at 760 mm. pressure. Water expands on freezing, 10 c.c. of the liquid becoming about 10.9 c.c. of ice. At about 4° C., water is at its maximum density. Its relative density at this temperature is taken as 1.

Water is a poor conductor of heat and of the electric current.

45. Steam and its Dissociation. — *Steam*, which is water in the condition of a vapor, is nine times as heavy as hydrogen. It is so stable that it does not begin to decompose into its elements until it is heated to about 1000° C. Above 1000° C. *the amount of decomposition increases with the temperature*, until at 2500° C. about half of the steam is no longer steam, but oxygen and hydrogen *uncombined.* No matter how long steam is kept at 2500° C. it cannot be decomposed *completely*, for the reason that side by side with the decomposition of steam into hydrogen and oxygen there is a **recombination** of these elements to form steam. At every temperature, therefore, between 1000° C. and the (high) temperature at which the decomposition of steam is complete, a condition of *equilibrium* is soon reached, at which as much steam is *produced* in a given time as is *decomposed* in the same time. Hence the change proceeds no farther unless the temperature is raised. If the temperature is lowered, enough hydrogen and oxygen recombine to produce equilibrium at the lower temperature.

A decomposition like that of steam is called a **dissociation.**

46. Action of Sodium upon Water. — In the first chapter reference was made to the action of sodium upon water as a means of preparing hydrogen. This reaction will now be considered more fully.

Sodium is a soft solid, somewhat lighter than water. It has a silvery luster *when freshly cut*, but tarnishes quickly in ordinary air. It is, therefore, kept under ligroin or kerosene. Although we commonly think of a metal as hard and heavy, sodium, which has neither of these properties, is yet one of the best representatives of the class of metals. This is due to its *chemical* properties, the most important of which, for our present purpose, is its behavior toward water.

When a piece of sodium is thrown upon water (this is done at arm's length to avoid danger from spattering), it at once attacks the water, melts, assumes a globular form, and then swims about until dissolved. If a lighted match is held near the sodium while it is floating upon water, a flame will appear; this is burning hydrogen. The hydrogen may be collected by placing the sodium in a short piece (1 cm. long) of glass tubing, and then plunging it quickly by the aid of tongs under the mouth of a bottle, or a test tube, filled with water and inverted in a pan of water.

Water in which a sufficient quantity of sodium has dissolved possesses *new properties*. It feels *soapy* to the touch, has a *bitter taste*, and turns many vegetable colors, e. g., *red* litmus to *blue*. If the water is evaporated, a white substance will remain, which is *sodium hydroxide*, or *caustic soda*. It is this substance that gives the water its new properties.

47. Quantitative Study of the Reaction; Hydroxides. — Sodium hydroxide is, as its name indicates, a compound of sodium, hydrogen, and oxygen. Since sodium hydroxide contains hydrogen, it is evident that not all of the hydrogen of water is set free by sodium. As a matter of fact, *only one-half of the hydrogen is so liberated*, the remaining half being in combination with sodium and oxygen. This appears from a quantitative study of the reaction.

If 23 grams of sodium had been placed in contact with a quantity of water greater than 18 grams, it would have acted upon 18 grams of water only, and would have formed 40 grams of sodium hydroxide, and, at standard temperature and pressure, a little over 11 liters of hydrogen. The hydrogen formed would weigh practically 1 gram. To summarize the results of the reaction, *quantitatively* as well as *qualitatively*: —

23 grams of sodium and 18 grams of water react to give 40 grams of sodium hydroxide and 1 gram of hydrogen.

As we have already learned, 18 grams of water consist of 2 grams of hydrogen and 16 of oxygen. Furthermore, 40 grams of sodium hydroxide would give, when decomposed, 23 grams of sodium, 16 grams of oxygen, and 1 gram of hydrogen. It is evident, therefore, that sodium replaces only *half* of the hydrogen of water in forming sodium hydroxide.

If we had used the metal *potassium*, the results would have been similar, viz.: —

39 grams of potassium and 18 grams of water react to produce 56 grams of potassium hydroxide and 1 gram of hydrogen.

The 56 grams of potassium hydroxide consist of 39 grams of potassium, 16 grams of oxygen, and 1 gram of hydrogen. Here again *one-half of the hydrogen* of the water decomposed is *liberated;* and the remaining half is retained in the hydroxide. In fact, *the hydroxides of all of the metals may be considered to be water with half of its hydrogen replaced by a metal.*

48. The Action of Metals upon Hydroxides. — By the use of proper methods, the hydrogen of sodium hydroxide may be replaced by sodium, and that of potassium hydroxide by potassium. The resulting substances will be *sodium and potassium oxides.* The reactions take place as follows: —

40 grams of sodium hydroxide and 23 grams of sodium give 62 grams of sodium oxide and 1 gram of hydrogen.

Also, 56 grams of potassium hydroxide and 39 grams of potassium give 94 grams of potassium oxide and 1 gram of hydrogen.

To replace the hydrogen of sodium hydroxide by sodium, and that of potassium hydroxide by potassium is a somewhat difficult operation; but it is very easy to replace the hydrogen of these hydroxides by aluminum. The resulting substances are *sodium-aluminum oxide* and *potassium-aluminum oxide* * respectively. These compounds are similar to sodium oxide and to potassium oxide in that they are *water with* all *of its hydrogen replaced* — in two stages — *by metallic elements.*

All of the facts just stated are given in the following recapitulation: —

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* Cf. *aluminates*, § 424.

	HYDROGEN.	OXYGEN.	SODIUM.	POTASSIUM.
18 parts by weight of water consist of	2	16		
40 parts by weight of sodium hydroxide consist of	1	16	23	
62 parts by weight of sodium oxide consist of		16	46	
56 parts by weight of potassium hydroxide consist of	1	16		39
94 parts by weight of potassium oxide consist of		16		78

49. Water in Combination. — Water is widely distributed, not only in the free condition, but also in combined form. Most natural substances contain it. This is true not only of animal and plant tissues and products, but even of *inorganic* substances. For convenience, we may distinguish at least three ways in which water may be contained in other substances: —

(1) Mechanically enclosed.
(2) As "water of crystallization."
(3) As an integral part of the substance.

The *form* in which water is contained in a substance generally appears from the behavior of the substance when heated.

50. Water Mechanically Enclosed. — Water may be held mechanically either (1) *between the crystals* of a substance, or (2) *in its pores.* In either case the water is given off when the substance is heated gently. When the substance contains water enclosed between crystals, however, the water escapes *explosively;* for the crystal-mass is broken in pieces by the steam produced.

Such substances are said to **decrepitate.**

Illustrations are : Common salt and potassium sulphate.

51. Water of Crystallization. — By *water of crystallization*, or *crystal-water*, we mean the water with which some substances combine when they crystallize from aqueous solution.

When substances containing water of crystallization are heated, they usually *melt* while the water escapes, and then assume the solid form again.

The loss of crystal-water by a substance is accompanied by a loss of crystalline structure and by other changes in properties. Thus, *cupric sulphate* is a white solid, but ***blue vitriol***, its ordinary form, is cupric sulphate *plus* water of crystallization. Crystallized sodium sulphate, sodium carbonate, alum, etc., all contain much crystal-water.

The amount of crystal-water which will combine with a given weight of the *anhydrous* (*i.e.*, water-free) substance is definite for each substance. Thus, 90 grams of water are united with 159 grams of cupric sulphate in every 249 grams of blue vitriol.

The color of a substance is usually the same when the substance is combined with water of crystallization as when it is in solution in water.

By no means *all* crystalline substances contain crystal-water. Cane sugar, salt, potassium sulphate, etc., crystallize from their solutions in water without taking up any of the water as crystal-water.

52. Water an Integral Part of the Substance. — Many substances which cannot be said to contain *water*, yet contain hydrogen and oxygen in the proportion in which these elements are united in water. Such compounds are the substances referred to as having water in the *third* form of combination, viz., *as an integral part of the substance.* Examples are sugar, starch, cotton, wood, etc. When these substances are heated, they are easily *decomposed*, liberating water and other products, while a residue of *charcoal* remains behind.

53. Efflorescence, Deliquescence, Etc. — Certain substances give up all or part of their crystal-water when exposed to the air, and thus lose their crystalline form. Such substances are said to **effloresce.**

An example is *crystallized* sodium carbonate, which becomes a non-crystalline powder when exposed to the air.

Certain other substances, on the contrary, when deprived of their water of crystallization, take it up again by absorbing water from the air and from other substances. Such bodies make good **dehydrating,** i. e., *drying,* **agents.**

Examples are: *Anhydrous* cupric sulphate and *anhydrous* potassium carbonate.

If dehydrating agents absorb so much water from the air that they *dissolve* in the water, they are said to **deliquesce.**

An example is *anhydrous* calcium chloride.

In any case, *if a substance takes up water* when exposed to moist air, it is said to be **hygroscopic.**

Many substances are drying agents, not because they tend to take up water of crystallization, but because they combine with water to form other compounds. *Quicklime,* which is calcium oxide, is an example. When this substance is *slaked,* by addition of water, it becomes calcium hydroxide.

54. Exercises.

1. How many grams of water are formed by the combustion of 10 grams of hydrogen in air?
2. What evidence is there that the hydrogen of water is more divisible than the oxygen?
3. How could you determine approximately how much water is contained in a potato?

4. 5 grams of crystalline barium chloride lost, when heated at 120° C., 0.65 grams. What per cent of water did it have?

5. Calculate the per cent of water of crystallization in a sample of potash alum, 47.4 grams of which lost 21.6 grams of water.

6. How many grams of water can be decomposed by 10 grams of sodium? How much sodium hydroxide will be formed?

7. How many grams of potassium are required to give with water 50 grams of potassium hydroxide? How many grams of hydrogen will be liberated at the same time? How many liters when 1 liter weighs 0.09 grams?

8. How many grams of water are formed by burning 10 liters of hydrogen when 1 liter of the latter weighs 0.085 grams?

CHAPTER IV.

SOLUTION.

55. **The Character of Solution.** — *Solution*, or dissolving, takes place when substances are mixed in such a way that *the matter of each is distributed uniformly through that of the others.* The resulting homogeneous mixture is called *a* solution. Thus broadly defined, the term solution includes phenomena called by many different names, but we shall restrict it to the absorption of a gas, liquid, or solid, within the portion of space occupied by some liquid. The liquid is called the **solvent.** Examples of common solvents are: *Water*, *alcohol*, and *ether*.

If the solvent is colorless, and the dissolved substance has a definite color, the solution will usually be colored; if the dissolved substance is white, or colorless, the solution will be colorless; but in any case the solution will be *clear*. Insoluble substances often remain mechanically *suspended* in a liquid for some time. Their presence is shown by the *turbid* appearance of the liquid.

Dilute solutions have practically the same volume as that of the solvent, but when the amount of dissolved substance becomes large, the volume of the solution is increased.

An illustration of the first statement is found in the familiar experiment in which a considerable quantity of powdered sugar is added, little by little, to a vessel entirely full of water without causing an overflow, while a much smaller amount of an insoluble substance, *e. g.*, sand, causes some of the water to be displaced.

56. Boiling Point and Freezing Point of a Solution. — Substances in solution raise the boiling point, and lower the freezing point of the solvent. Thus, water containing salt or sugar boils above 100° C. at 760 mm. pressure, and freezes below 0° C. In *dilute* solutions the rise of the boiling point and the lowering of the freezing point are *proportional to the amount of dissolved substance* in a given volume. The specific gravity of solutions of solids is greater than that of the solvent. Thus, sea water has a specific gravity of 1.026.

57. Temperature Changes during Solution. — When a *gas* dissolves in a liquid there is, as a rule, an evolution of heat and a consequent rise of temperature, but the solution of a *solid* is usually attended by an absorption of heat and a reduction of temperature. Some solids, however, dissolve in water with evolution of heat. Examples are: Anhydrous calcium chloride and anhydrous sodium carbonate. These apparent exceptions are usually substances that have been deprived of water of crystallization, and take it up again when brought into contact with water. Because of the heat evolution due to the union of these substances with their crystal-water, the heat absorption due to the solution of the crystallized substances is not perceptible. When the *crystals* of such substances are dissolved in water there is usually a reduction of temperature.

58. Solubility. — By the *solubility* of a substance we mean the *maximum* amount of the substance that can be taken up by a given quantity of the solvent *under the given conditions.*

The amounts of two substances which will dissolve in a given weight of a solvent are very unequal, as are, also, the quantities of two solvents which are required to absorb a given weight of the same substance. Thus, sugar and salt are very soluble in water, but practically insoluble in ether. Even in water, however, their solubilities are very different, sugar being much more soluble than salt. Similar differences exist in the case of gases, hydrogen, for example, being only about half as soluble as oxygen in water of the ordinary temperature.

59. Effect of Temperature on Solution. — The solubility of a substance depends not only upon the solvent used, but also upon the *temperature.* As a rule, solids are more soluble in hot than in cold liquids, while the reverse is true of gases. The following table shows the effect of temperature upon the solubility of several solids.

SUBSTANCE.	GRAMS SOLUBLE IN 100 GRAMS WATER.		
	At 0° C.	At 20°.	At 100°.
Potassium nitrate.	13.3	31.7	246.
Sodium chloride.	35.	36.	39.7
Potassium chlorate.		7.2	59.5
Cupric sulphate (cryst.).		42.3	203.3

To illustrate the decrease of solubility of gases with rise of temperature we may take the case of oxygen, 4.1 c.c. of which can dissolve in 100 c.c. of water at 0° C., 2.9 c.c. at 15°, and *none* at 100°.

60. Soluble and Insoluble Substances. — A solid requiring less than 100 times its weight for complete solution may be considered *readily* soluble; one needing between 100 and 1,000 times its weight, *difficultly* soluble; while one which requires more than 1,000 parts of the solvent may be called *insoluble.*

There is, however, a great difference in the solubilities of so-called "insoluble" substances. Thus, strontium sulphate requires about 8,000 parts of water for solution, and barium sulphate, about 400,000 parts.

We call a substance *insoluble*, then, only *relatively* to other substances, and not absolutely, for *there is prob-*

ably no substance of which a small amount will not dissolve, if the quantity of the solvent is very large.

61. Saturated Solution. — When a liquid has in solution all that it can hold of a substance under certain conditions, it is said to be *saturated* with respect to that substance *under the specified conditions*. Considering now only the solution of solids in liquids, we may know that a solution is saturated when a slight lowering of its temperature or the removal of a small amount of the solvent, *e. g.*, by evaporation, causes *precipitation* of some of the dissolved substance.

There are two methods in common use for the production, at ordinary temperatures, of a saturated solution of a solid. In the first of these the solvent is allowed to remain for some time in contact with an excess of the solid, and the mixture is shaken or stirred to hasten solution.

In the second method, the solvent is heated above the ordinary temperature with enough solid to produce saturation at the higher temperature, and the solution is then cooled to the ordinary temperature. In this way, the excess of solid is deposited.

62. Supersaturated Solutions. — Many solutions, however, although saturated at temperatures above the ordinary, will not deposit their excess of dissolved solid when the temperature is lowered. Such solutions are said to be **supersaturated.** A solution usually remains supersaturated only while undisturbed. If the containing vessel is jarred, or if small particles, *e. g.*, of dust, are introduced, precipitation often results. *The most certain way*, however, of disturbing a supersaturated solution is to add a crystal of the dissolved substance. A rapid separation of the excess of the latter is the result.

63. Precipitation and Crystallization. — As stated in the preceding section, a solid may be made to separate from its solution, if the latter is brought to the point of saturation. A dilute solution must, therefore, be *concentrated* if separation is to take place. If a solid separates from solution rather slowly, it will frequently be found to consist of regular masses called *crystals. The more slowly crystallization takes place, the larger and more perfect will the crystals be.* But often a solution is brought to saturation *suddenly*, as is the case when the temperature of an almost saturated solution is rapidly lowered, or when another solvent is added, or when a new substance is formed which is not very soluble in the solvent. In such cases, the substance that separates from solution will consist of very *small* crystals, or it may even be in an *amorphous*, i. e., non-crystalline, form. In either case it is called a **precipitate.**

Thus, when silver nitrate and sodium chloride solutions are mixed, there is produced a white, amorphous precipitate of silver chloride, the sodium nitrate formed at the same time remaining in solution. Relatively to silver nitrate solution, therefore, sodium chloride solution is a **precipitant,** since its addition produces a *precipitate.*

64. Decantation and Filtration. — We may separate a precipitate from the solution in which it is suspended either by allowing it to settle and then *decanting*, i. e., pouring off, the clear solution, or by *filtering* the mixture of liquid and solid. For the latter purpose we use a *filter paper*, consisting of cellulose, which permits liquids and *dissolved* solids to pass through its pores, but usually holds back *suspended* solids. What passes through the filter is called the **filtrate.**

65. Crystallization from Fusion. — A solid may separate in crystalline form not only from solution, but also *by the solidification of a liquid*, i. e., from *fusion.* Thus, water freezes, and molten sulphur solidifies, *in crystalline form.*

Just as there is a *supersaturated* condition of some solutions, owing to a tardy separation of dissolved solids, so there is a *superfused* condition of some liquids, because of their slow assumption of the solid form even at temperatures below their true freezing points. Crystallization is effected in the same way in both cases, viz., by "*inoculation*" with a crystal of the solid.

66. Effervescence. — Gases, like solids and liquids, separate from solution if formed in a solvent unable to hold them. Because of their low specific gravity, however, gases rise to the *top* of the solution, and thus escape into the air. A liquid evolving a gas is said to **effervesce.**

The action of zinc on dilute sulphuric acid, for example, causes *effervescence* of the dilute acid, owing to the escape of hydrogen. Similarly, "soda water" effervesces, because of liberation of carbon dioxide gas.

67. Exercises.

1. Why do subterranean waters contain more gaseous substances in solution than surface waters?

2. Why is it that insoluble substances, *e. g.*, sand, "burnt" alum, etc., have no taste?

3. Suggest a method of separating a mixture of potassium nitrate and sodium chloride so as to recover almost all of the nitrate. See the table of solubilities in § 59.

4. Why does "spattering" take place in the evaporation to dryness of a solution of common salt, etc.?

5. How could you separate a mixture of white sand and common salt so as to recover all of each in a dry condition?

6. Calculate the parts per cent of potassium dichromate present in a solution containing 120 grams of water and 15 grams of the dichromate.

CHAPTER V.

FUNDAMENTAL LAWS CONCERNING NUMBERS AND NOMENCLATURE.

56. Persistence of Mass. — The fundamental fact regarding every chemical change is that it results in the formation of at least **one new substance.** If the new substance is an element it can have been formed only by the decomposition of some previously existing compound; if a compound, only by the union of certain elements. Thus considered, *every chemical reaction is merely a change in the relations between elementary substances.*

Most of the reactions already studied may, in fact, be classed under one of three heads: —

1. *Elements in combination become separated* by a change in conditions; as when mercuric oxide was decomposed by heat into mercury and oxygen.

2. *Elements* (or an element and a compound) *existing apart united to form a* (or another) compound; as when hydrogen and oxygen combined to form water.

3. *A free element took the place of one of the elements of a compound,* the latter element being thereby freed from combination. An illustration is the case of zinc and dilute sulphuric acid. Here hydrogen is set free from the acid, and zinc enters into combination in the place of the hydrogen.

Since, therefore, [illegible] of the reacting substances [illegible] of the [illegible] of the products. [illegible] of Mass,' or 'Conservation of Matter.' It has proved [illegible] to be true in every case that has been examined.

II. Constant Proportions. — [illegible] 'Constant Proportions by Weight.' [illegible] the products [illegible]

[illegible] always [illegible] grams of [illegible] hydrogen [illegible]

Another way in which [illegible] given chemical compound [illegible] always be found to be composed [illegible] in the same proportions.

[illegible] determinations of the composition of [illegible] [illegible] and oxygen [illegible] and [illegible] and oxygen [illegible].

70. Symbols and Formulas.—In all the reactions [illegible] we have written out in full the names of the substances taken and obtained, together with the proportions by weight of each. As a rule, however, [illegible] *symbolic expressions* in place of the full names of substances. When this method is once understood, it will be seen to have many advantages. As has already been stated in the introductory chapter, the elements are represented by *symbols*.

A symbol is simply the initial letter, or the initial followed by another characteristic letter, of the name of the element. We indicate the composition of a compound substance by writing the symbols of the elements which make up the compound side by side, without an intervening sign ([illegible], ⟶, or =). The resulting expression is called a *formula.*

Thus, mercuric oxide, a compound of mercury and oxygen, is represented by the formula HgO. Similarly, HCl represents a compound of hydrogen and chlorine, *i. e.*, hydrochloric acid.

71. Symbolic Equations. A symbolic equation (called, simply, "*an equation*") is formed by writing, instead of the names of the reacting substances, their symbols and formulas. Thus, the fact that sodium acts upon water to produce sodium hydroxide and hydrogen is shown by the expression,

$$Na + HOH \text{ (or } H_2O) \longrightarrow NaOH + H.$$

In this equation Na is the symbol of sodium; H, that of hydrogen; and O, that of oxygen. The formula HOH, or H_2O, for water, shows that water is composed of hydrogen and oxygen, while the formula NaOH, for sodium hydroxide, shows that sodium hydroxide is a compound of sodium, oxygen, and hydrogen. The sign ⟶ (or =) is best read "gives" or "produces." The sign + is read "and." The symbols and formulas of the equation are read in the direction of the arrow ⟶; those preceding the arrow are called the *factors*, those succeeding it the *products* of the reaction. When the sign = is used, the symbols and formulas to the left of it are the factors, and those to the right the products.

Among the advantages of the use of symbols are the following: —

1. *Symbolic expressions for compounds enable us to see, at once, what elements make up the compounds.* Thus, while the common names of *salt, water, galena,* and *caustic soda* give us no idea of the composition of these bodies, the corresponding formulas, NaCl, H_2O, PbS, and NaOH, do.

2. *Symbolic equations, if correctly written, enable us to determine what changes in the relations of elements have resulted from a given case of chemical action.* Thus it requires only a glance at the symbolic equation for the action of sodium upon

water to determine that in this reaction sodium displaced part of the hydrogen of water to form sodium hydroxide.

72. Equations the Result of Experiment. — *Equations mean nothing unless they are the result of experiment.* If the student cannot himself prove what products are formed in a reaction, he must depend upon some trustworthy source, *e. g.*, the teacher or a text-book, for the necessary information. The student should learn the important equations given from time to time in the text, not by rote, but with appreciation of their meaning. He will soon find that the number of equations that must actually be memorized is small, for, with a few typical equations as a basis, a large number of analogous ones can readily be acquired.

73. Quantitative Meaning of Symbols and Equations. — The equation

$$Na + H_2O \longrightarrow NaOH + H$$

means to the chemist much more than has been stated in § 70, *for it indicates the proportions by weight of the reacting substances and of the products.* We can give this added meaning to the above and to every equation by letting the symbol of each element represent not only the element in general, but also a *definite mass* of it. The formula of a compound will then show not only what elements are contained in the compound, but, in addition, *the proportions by weight in which they are united.* Finally, if we assume that symbols and formulas stand for definite masses of elements and of compounds, respectively, then *the equation for every reaction will represent the proportion by weight of every substance entering into the reaction.*

Thus, the equation

$$Na + H_2O \longrightarrow NaOH + H$$

means to the chemist that 23 parts by weight of sodium react with 18 parts of water to produce 40 parts of sodium hydroxide and 1 part of hydrogen. Of course the proportions will be true, whatever units are used, *i. e.*, with pounds and tons as well as with milligrams and grams, but for our present purpose we will let symbols and formulas represent *grams*. Na means, therefore, 23 *grams* of sodium, and H_2O, 18 *grams* of water. Since water is one-ninth hydrogen and eight-ninths oxygen, 18 grams of water must contain 2 grams of hydrogen and 16 of oxygen. O, therefore, means 16 grams of oxygen.

74. How to Represent Multiples of Symbols and Formulas. — In the formula H_2O, H_2 means *twice* the quantity of hydrogen represented by H, for in all chemical formulas a small figure written *after* and *slightly below* a symbol multiplies the quantity represented by the symbol *immediately preceding.*

The formula NaOH means 40 grams of sodium hydroxide. Of the 40 grams, 23 are sodium, 16 are oxygen, and 1 is hydrogen. The equation thus accounts for every gram of material taken: —

$$\begin{array}{lcl} Na + H_2O & \longrightarrow & NaOH + H. \\ 23 + (2 + 16) & & (23 + 16 + 1) + 1 \end{array}$$

If we multiply the quantities taken in the above equation by 2, the *relative* amounts are not altered. Thus the equation $2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2$ represents all the facts *as well*, at least, as the simpler equation.

A figure written *before* a formula multiplies the quantity of the substance represented by the formula, just as the small figure written *after* a symbol multiplies the quantity indicated by the symbol.

Therefore 2 Na means 46 ($= 23 \times 2$) grams of sodium; 2 H_2O means 36 ($= 2 [2 + 16]$) grams of water; 2 NaOH means 80 ($= 2 [23 + 16 + 1]$) grams of sodium hydroxide; and H_2 means 2 grams of hydrogen.

It often happens that a formula contains a *group* of elements repeated two or more times. Thus, the formula of calcium hydroxide is $Ca(OH)_2$; it may also be written CaO_2H_2; or, better still, $Ca\genfrac{}{}{0pt}{}{OH}{OH}$. In the first of these formulas, viz., $Ca(OH)_2$, *the small figure written after the parenthesis multiplies what is in the parenthesis immediately preceding*, just as if the symbols in the parenthesis were together *one symbol*. Symbols which are grouped together in this way are called *radicals*.

Other examples of formulas containing radicals are: $Cu(NO_3)_2$ for cupric nitrate, and $Fe_2(SO_4)_3$ for ferric sulphate. These might be written CuN_2O_6 and $Fe_2\ S_3O_{12}$, respectively, but the first formulas are preferable because they enable us to see that the compounds are derived from nitric acid and sulphuric acid, HNO_3 and H_2SO_4, respectively, while the second formulas do not.

The water of crystallization present in many compounds is represented by the formula of water (taken the necessary number of times) *after* the formula of the compound. Thus, while $CuSO_4$ stands for *anhydrous* cupric sulphate, *blue vitriol* has the formula $CuSO_4 . 5\ H_2O$; crystallized zinc sulphate is $ZnSO_4 . 7\ H_2O$; and crystallized sodium sulphate (Glauber's salt) is $Na_2SO_4 . 10\ H_2O$.

75. Combining Proportions. — The following list gives the names of some of the more *important* elements, and *the proportions by weight*, or a sub-multiple of them, *in which these elements unite* when they form compounds.

ELEMENT.	SYMBOL.	COMBINING PROPORTION.	ELEMENT.	SYMBOL.	COMBINING PROPORTION.
Aluminum.	Al.	27.	Manganese.	Mn.	55.
Barium.	Ba.	137.	Mercury.	Hg.	200.
Bromine.	Br.	80.	Nitrogen.	N	14.
Calcium.	Ca.	40.	Oxygen.	O.	16.
Carbon.	C.	12.	Phosphorus.	P.	31.
Chlorine.	Cl.	35.5	Potassium.	K.	39.
Copper.	Cu.	63.	Silicon.	Si.	28.
Fluorine.	Fl.	19.	Silver.	Ag.	108.
Hydrogen.	H.	1.	Sodium.	Na.	23.
Iodine.	I.	127.	Strontium.	Sr.	87.
Iron.	Fe.	56.	Sulphur.	S.	32.
Lead.	Pb.	207.	Tin.	Sn.	118.
Magnesium.	Mg.	24.	Zinc.	Zn.	65.

76. The Use of Combining Proportions. — The derivation of the combining proportions given above is of great importance to Chemistry; however, it depends upon facts which we are not ready to consider at this time. For the present, the combining proportions given in the preceding table will enable us to use *equations, formulas, and symbols quantitatively.*

Thus, if the formula MgO is given to the compound which magnesium forms when it burns in oxygen, a reference to the table will show that in this compound magnesium and oxygen are united in the proportion of 24 grams of magnesium to 16 grams of oxygen. From 24 grams of magnesium, therefore, we can get 40 grams of magnesium oxide. Again, if Al_2O_3 represents correctly the composition of aluminum oxide, the student can see readily that, in this compound, aluminum and oxygen are combined in the proportion of 54 grams of aluminum to 48 of oxygen.

The equation $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$ thus means, as the result of a simple calculation, that 65 grams of zinc react with 98 grams of sulphuric acid to give 161 grams of zinc sulphate and 2 grams of hydrogen.

77. How a Compound of Two Elements is Named. — *A compound of two elements has the name of each appearing in its name*, but the last syllable of the name of one of the elements is changed to **ide**.

Thus *sodium chloride* is a compound of sodium and chlorine; *magnesium oxide*, one of magnesium and oxygen (here the *y* before the *ide* is omitted); *calcium carbide*, one of calcium and carbon; and *lead sulphide*, one of lead and sulphur.

As to which element shall have the ending *ide*, the rule is as follows: If one of the elements is an undoubted *metal*, it retains its full name, as in the cases given above, and *the ending of the non-metal is changed to* **ide**. If neither is a metal, as in the case of a compound of sulphur with oxygen, the name of the one having the smaller resemblance to a metal is changed to *ide*. Thus, a compound of sulphur with oxygen is called *sulphur oxide*, but one of sulphur and hydrogen is called *hydrogen sulphide*. (N. B. Hydrogen has certain *metallic* properties.) If both elements were metals, the same rule would hold, and the one which possessed the less *characteristically* metallic properties would have its ending changed to **ide**.

78. How to Distinguish between Compounds of the Same Two Elements. — If there is *more than one* compound of the same *two* elements, the ending of the less metallic element is changed in each case, as before, to *ide*, but the compounds are distinguished from one another in one of two ways. These are, —

(1) **By changing the final syllable** of the more metallic (*i. e.* electro-positive) element; or,

(2) **By placing a prefix** before the name of the less metallic (*i. e.*, more electro-negative) element.

By the *first* method the ending of the metallic element is changed to *ous* or *ic*, as, for example, in the names of the two compounds of mercury and chlorine, which are called mercur*ous* chloride and mercur*ic* chloride, respectively. The ending *ous* is given to that one of the compounds which contains the *larger* proportion of the metallic element (here mercury); the ending *ic*, on the other hand, to the one containing the smaller proportion of the metallic element.

Ous means in chemical phraseology, as in ordinary language, "full of" or "containing much of." The appropriateness of the names for the two compounds of mercury and chlorine will be seen by a comparison of the proportionate amounts of the elements in the two compounds. Thus, mercurous chloride, $HgCl$, has 200 parts by weight of mercury to 35.5 of chlorine, while mercuric chloride, $HgCl_2$, has 200 of mercury to 71 of chlorine. The larger proportion of mercury is, evidently, in the mercurous compound.

In the case of some elements, *e. g.*, copper and iron, the *Latin* names are used, and the ending is applied to these rather than to the English names. Thus, the two common copper oxides are, —

(*a*) Cupr*ous* oxide, containing copper, 63 parts, to oxygen, 8 parts ;

(*b*) Cupr*ic* oxide, containing copper, 63 parts, to oxygen, 16 parts.

Similarly, iron compounds are distinguished by the names, —

(*a*) Ferr*ous* oxide, chloride, etc., for the compound containing the larger proportion of iron: and

(*b*) Ferr*ic* oxide, chloride, etc., for the one containing the smaller proportion of iron.

A *second* way of distinguishing between two (or more) compounds of the same two elements is to apply a *numerical prefix* to the *less metallic* element and to leave the metallic element unchanged. Thus the names carbon *mon*oxide and carbon *di*oxide distinguish the two compounds of carbon and oxygen from each other.

The prefix *mon* means "one" or "first," referring to the formula CO, while *di* means "two" or "second," referring to the formula CO_2.

In a similar way we distinguish sulphur *dioxide*, SO_2, from sulphur *trioxide*, SO_3.

79. Exercises.

1. Calculate the percentage composition of sulphuric acid, sodium hydroxide, manganese dioxide (MnO_2), and potassium chlorate ($KClO_3$).

2. What relative quantities of the substances taken and produced are indicated in the equations,

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2, \text{ and}$$
$$2\,K + 2\,H_2O \longrightarrow 2\,KOH + H_2\,?$$

3. What quantity of hydrogen could be obtained from the action of 50 grams of potassium upon an excess of water?

4. Calculate the parts per cent of water of crystallization in blue vitriol, in Glauber's salt, and in gypsum, $CaSO_4 . 2\,H_2O$.

5. What weight of anhydrous zinc sulphate is contained in 75 grams of the crystallized form, $ZnSO_4 . 7\,H_2O$?

6. How many grams of phosphorus must be burned to produce 60 grams of phosphorus pentoxide, P_2O_5?

7. Name the compounds having the formulas CO, CS_2, $ZnCl_2$, HgI, and BaC_2.

CHAPTER VI.

CHLORINE.

80. Existence. — Chlorine is a heavy, greenish-yellow gas, of irritating odor and poisonous properties. It was discovered by the Swedish chemist Scheele in 1774, but was not generally considered to be an element until 1809.

Because of its great *reactivity*, i. e., its tendency to act chemically with other substances, chlorine is not found in nature *free*, but always in combination with other elements. Its most abundant compounds are sodium, potassium, and magnesium chlorides and hydrochloric acid, which is hydrogen chloride. Sodium chloride is common salt.

81. Common Method of Preparation. — Chlorine is usually prepared by the action of reagent hydrochloric acid upon manganese dioxide. The apparatus is shown in Fig. 19.

A flask containing manganese dioxide (MnO_2) in small lumps is provided with a thistle tube and a delivery tube, and is supported so that it may be warmed in a water bath. Concentrated hydrochloric acid is added through the thistle tube, and the evolution of chlorine begins. The gas is allowed to pass through a wash bottle containing a little water, a drying bottle one-third full of concentrated sulphuric acid (a U-tube of calcium chloride may be used instead), and then into a collecting bottle, the air of which is to be displaced by chlorine. From the collecting bottle a delivery tube reaches beneath the surface of a solution of sodium hydroxide, which absorbs any escaping chlorine, and enables us to know when the air in the apparatus has been displaced. When a collecting bottle is full of chlorine it is removed and stoppered, and replaced by another bottle until enough gas has been obtained. The bath of hot water is now replaced by one of cold water, and the evolution of chlorine is thus stopped.

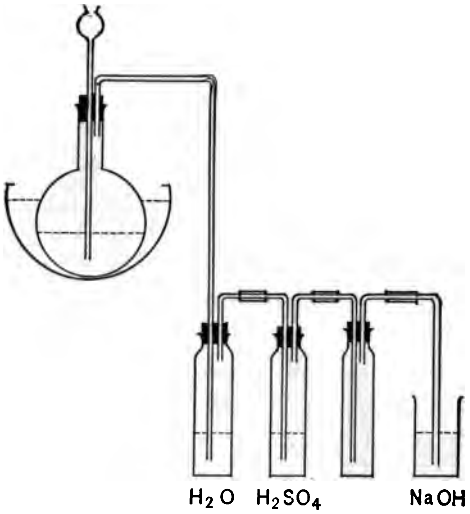


FIG. 19.

The proportions by weight of the *factors*, manganese dioxide and hydrochloric acid, and of the *products* resulting from their action on one another are as follows: —

87 grams manganese dioxide and 146 grams hydrochloric acid (in aqueous solution) give 71 grams chlorine, 126 grams manganous chloride, and 36 grams water. The same facts are represented by the equation,

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2.$$

It is probable that the reaction takes place in two stages, and that manganese tetrachloride, $MnCl_4$, is formed first and then breaks down into manganous chloride and chlorine. Equations representing these facts are: —

$$(1)\ MnO_2 + 4\,HCl = MnCl_4 + 2\,H_2O.$$
$$(2)\ MnCl_4 = MnCl_2 + Cl_2.$$

The *final* result, in any case, is that shown in the equation given above.

Instead of manganese dioxide and hydrochloric acid, a mixture of common salt, manganese dioxide, and sulphuric acid is often used. The result is approximately the same, however, for common salt and sulphuric acid give by their action hydrochloric acid.

82. Other Methods. — Manganese dioxide is not the only substance that will liberate chlorine from hydrochloric acid; *potassium dichromate*, $K_2Cr_2O_7$; *potassium chlorate*, $KClO_3$; *nitric acid*, HNO_3, and many other substances will do it.

water bath to 30° C., while the other end is surrounded by a freezing mixture of ice and salt. After a short time, liquid chlorine will condense at the drawn-out end. The gas has been liquefied by its own pressure. This experiment can be carried out only in a strong tube securely sealed.

Liquid chlorine is an article of commerce; it is stored and transported in iron cylinders.

84. Chemical Properties. — Chlorine is a very dangerous substance to inhale, and should, therefore, be generated only in a gas chamber, or where there is a good draught. If it has been taken into the lungs, alcohol or ammonia should be inhaled to counteract it.

It is always well to sprinkle a little ammonia water about in the neighborhood of a chlorine generator.

Chlorine is intensely active toward many other elements, forming, by direct union with them, the *chlorides.* Many substances that combine with oxygen slowly, or not at all at ordinary temperatures, unite readily with chlorine. Powdered antimony and copper foil (the latter must be hot) *glow* when put into chlorine, the products being antimony trichloride ($SbCl_3$) and cupric chloride ($CuCl_2$) respectively. Sodium, tin, magnesium, and phosphorus all give corresponding *chlorides* when put into the gas. But it is toward hydrogen that chlorine shows its most remarkable behavior, for while the two gases do not combine at all in the dark, and only very slowly in diffused light, yet they unite with *explosive violence* in sunlight.

The mixture of hydrogen and chlorine may also be exploded by a burning match or by the electric spark.

Chlorine shows this tendency to combine with hydrogen not only when the hydrogen is in the free state, but also when it is united with other elements. As illustrations we may take the action of chlorine toward water, ammonia, and turpentine.

85. Action of Chlorine and Water. — The aqueous solution of chlorine may be preserved for a long time if kept cold and in the dark, but it decomposes rapidly in sunlight, giving as *final* products hydrochloric acid and oxygen. The equation is: —

$2\,H_2O + 2\,Cl_2 \longrightarrow 4\,HCl + O_2$. (See, however, "bleaching powder.") If the decomposition of chlorine water by sunlight is carried out in a long tube (Fig. 21), a colorless gas will collect in the upper part of the tube. The gas is oxygen. Much of this gas will also be found in the solution.

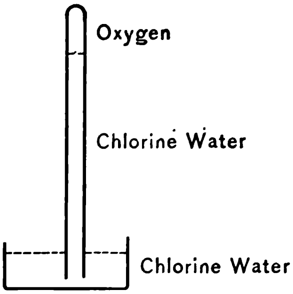


FIG. 21.

86. Action of Chlorine and Ammonia. — When the hydrogen of ammonia is appropriated by chlorine, hydrochloric acid and nitrogen are formed, as represented by the equation,

$$2\,NH_3 + 3\,Cl_2 \longrightarrow 6\,HCl + N_2.$$

With the excess of ammonia the hydrochloric acid gives *ammonium chloride*, NH_4Cl, the material of the white smoke seen when ammonia and chlorine gases come together.

87. Action of Chlorine and Turpentine.—The behavior of chlorine and turpentine may be shown by immersing a piece of filter paper in warm turpentine and then plunging it into a jar of chlorine. The turpentine soon ignites, and burns with a smoky flame. Turpentine is a compound of carbon and hydrogen, and the chlorine, by uniting with some of the hydrogen, but not with the carbon, sets the carbon free in the form of a dense, black smoke.

88. Uses of Chlorine. — Chlorine is used in large quantities as a **bleaching** and **disinfecting agent,** and is generally made for these purposes from *bleaching powder*, or "chloride of lime." Bleaching powder is a white substance formed by the action of chlorine upon "slaked" lime (calcium hydroxide), and is easily decomposed by acids, even by the carbon dioxide of the air, with evolution of chlorine. Fabrics to be bleached by the chlorine process are, therefore, immersed in a bath of dilute acid, and then in one of chloride of lime. In this way *chlorine is set free in immediate contact with the coloring matter of the cloth, and bleaches it.*

Chlorine is not a bleaching agent ordinarily, unless water is present, hence it is likely that chlorine itself does not act upon the coloring matter, but upon the water. As a result, oxygen is probably set free; and it is *oxygen*, and not chlorine, that bleaches the cloth. Since ordinary oxygen is not able to effect this change, we assume that oxygen at the instant of its liberation from water is in a condition different from that in which we ordinarily find it. We say that it is in a *nascent* condition. The reason for the peculiar behavior of an element in its nascent state will be given later.

Compared with the old bleaching process, which consisted in exposing the fabric to the oxidizing agents of the air, the chlorine method is of course very rapid, but, unfortunately, the bleaching agent used too often attacks the fiber of the cloth as well as its coloring matter. Hence delicate materials, such as the better grades of straws, laces, silks, and woolens, are usually decolorized by ***sulphur dioxide***, which, although it does not bleach so permanently as chlorine, has yet the advantage of acting less upon the fabric.

The action of chloride of lime as a disinfectant is similar to its action as a bleaching agent: *nascent oxygen* is formed, and this destroys the micro-organisms of the surrounding air.

89. Exercises.

1. How many grams of chlorine can, theoretically, be obtained by the electrolysis of 50 grams of hydrochloric acid?
2. How many grams of manganese dioxide are required to give with an excess of hydrochloric acid 10 grams chlorine?
3. What will be the volume of 40 grams chlorine under conditions at which 1 liter of hydrogen weighs 0.09 gram?
4. How much silver chloride, AgCl, can be formed by burning 54 grams silver in chlorine gas?
5. Calculate the per cent of chlorine in sodium chloride.
6. How many liters of chlorine can be made by the action of 25 grams of manganese dioxide with an excess of hydrochloric acid? (Assume that 1 liter of chlorine weighs 3 grams.)

CHAPTER VII.

HYDROCHLORIC ACID.

90. Existence. — Hydrochloric acid gas is colorless and heavy, fumes in moist air, and dissolves readily in water. It is found in only small amounts in nature, *e. g.*, in volcanic gases and in some springs. It makes up about 0.22 of 1% of the gastric juice.

91. Preparation: Common Laboratory Method. — Hydrochloric acid may be prepared readily by the action of sulphuric acid, H_2SO_4, upon common salt, NaCl. The apparatus is shown in Fig. 22.

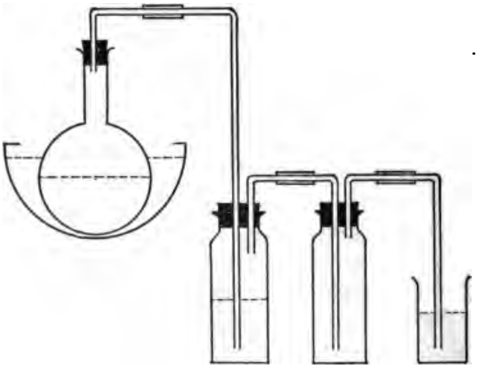


FIG. 22.

The flask contains common salt and sulphuric acid diluted with half its volume of water, and cooled. (Caution! *In di-*

luting sulphuric acid we always pour the acid into the water.) A hot-water bath serves to heat the flask. The first bottle contains concentrated sulphuric acid to dry the gas, and the second bottle is the collecting vessel. A beaker of water collects any escaping gas and shows when the gas in the collecting bottle is free from air.

The reaction between common salt and sulphuric acid takes place according to the equation,

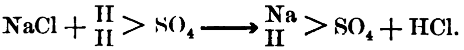
$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl;$$

that is to say, 58.5 grams of sodium chloride and 98 grams of sulphuric acid give 120 grams sodium hydrogen sulphate and 36.5 grams hydrochloric acid. If there is an *excess* of sulphuric acid, the sodium chloride is all used up, and the white solid which crystallizes in the generating flask when the latter cools is *sodium hydrogen sulphate.*

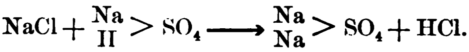
92. Commercial Manufacture of the Acid. — In the first stage of the manufacture of sodium carbonate (soda) by the "Le Blanc" process, sodium chloride is treated with sulphuric acid, with the results illustrated by the equation just given. Since, however, *sodium sulphate* (Na_2SO_4) and not *sodium hydrogen sulphate* is the product wanted, the sodium hydrogen sulphate is converted into sodium sulphate by heating it with more sodium chloride to a high temperature. The reaction which then takes place is represented thus: —

$$\begin{array}{llcll} NaCl + & NaHSO_4 & \longrightarrow & Na_2SO_4 + & HCl. \\ 58.5\text{ g.} & 120\text{ g.} & & 142\text{ g.} & 36.5\text{ g.} \end{array}$$

From this we see that *the hydrogen of sulphuric acid*, like that of water, *may be replaced in* **two** *stages;* for while at low temperatures only 58.5 grams of sodium chloride react with 98 grams of sulphuric acid, at a high temperature a *second* quantity of sodium chloride, equal to the first, is able to react, and thus produces a second quantity of hydrochloric acid. This will be more evident when the two equations are written together: —

(1) 

$$\mathrm{NaCl} + \begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix} > \mathrm{SO_4} \longrightarrow \begin{matrix}\mathrm{Na}\\ \mathrm{H}\end{matrix} > \mathrm{SO_4} + \mathrm{HCl}.$$

(2) 

$$\mathrm{NaCl} + \begin{matrix}\mathrm{Na}\\ \mathrm{H}\end{matrix} > \mathrm{SO_4} \longrightarrow \begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix} > \mathrm{SO_4} + \mathrm{HCl}.$$

The hydrochloric acid formed as a by-product in the soda manufacture is conducted into water, and the solution is sold as *commercial* hydrochloric or muriatic acid. It is usually colored by slight impurities.

93. Physical Properties. — Hydrochloric acid is about 1¼ times as heavy as air, and 18¼ times as heavy as hydrogen. It is very soluble, 505 c.c. being held by 1 c.c. water at 0° C. and 760 mm. pressure. The concentrated solution of the pure gas in distilled water at the ordinary temperature is the "*chemically pure*" (c. p.) **reagent** hydrochloric acid. This is a colorless liquid of specific gravity 1.2 (Water = 1). The concentrated solution of hydrochloric acid *fumes* strongly in moist air because the escaping gas condenses some of the water vapor of the air.

The dry gas can be converted into a colorless liquid at a low temperature and great pressure.

94. Volumetric Composition of Hydrochloric Acid.

— The composition of hydrochloric acid may be demonstrated in the same way as that of water, viz., **by electrolysis.** If an electric current of sufficient strength is passed through a concentrated aqueous solution of the acid, hydrogen is produced at the — electrode, and chlorine at the + electrode.

The gases collect at unequal rates, at first, because of the greater solubility of the chlorine; but when the liquid has become saturated with both gases the hydrogen and the chlorine gather in the collecting tubes at the same rate. See Fig. 23.

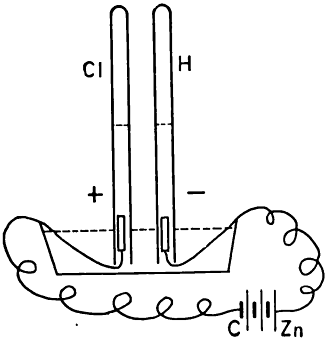


FIG. 23.

Therefore hydrochloric acid gas must be composed of hydrogen and chlorine *united in equal proportions by volume.*

The same fact may be proved **synthetically,** for if a mixture of hydrogen and chlorine be exploded, it will be found that equal volumes of the two gases have disappeared. The volume of hydrochloric acid formed will be equal to the sum of the uniting gases. These facts may be represented graphically as follows: —

□	+ □	⟶ □□
1 vol. hydrogen.	1 vol. chlorine.	2 vols. hydrochloric acid.

Note that this case is different from that of water; for, in the production of 2 volumes of steam, 2 volumes of hydrogen united with 1 of oxygen, *i. e.*, 3 volumes of the mixed gases gave only 2 volumes of the product.

Since the weights of equal volumes of hydrogen and chlorine are about as 1 : 35.5, the two volumes of hydrochloric acid formed by their union should be about 36.5 times as heavy as *one* volume of hydrogen. Hence hydrochloric acid should be about 18.25 (= 36.5 ÷ 2) times as heavy as hydrogen. This is actually the case.

That hydrochloric acid gas gives, when decomposed, one-half of its own volume of hydrogen, may be shown by the action of sodium. For convenience the sodium is diluted by *alloying* it with mercury.

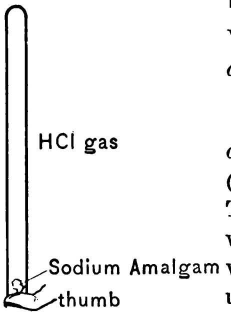


FIG. 24.

A small amount of the resulting *sodium amalgam* is put into a long measuring tube (Fig. 24) full of hydrochloric acid gas. The open end of the tube is then closed with the thumb, and the tube is shaken vigorously. When the thumb is removed under water, some of the water rushes up into the tube to replace the chlorine. If the water inside and outside the tube is now brought to the same level, the volume of the residual hydrogen will be found to be approximately *one-half* that of the hydrochloric acid taken.

95. Acid Properties. — In addition to the properties already given, hydrochloric acid (*i. e.*, the aqueous solution or the moist gas) has the characteristics of a special class of substances called **acids.** Acids may be described roughly as having a *sour* (acid) *taste*, the ability to change certain vegetable colors, e. g., *blue* or *purple* litmus to *red*, and also the power to *neutralize* the properties of another class of substances, viz., the **bases.** Thus the action of hydrochloric acid upon *sodium hydroxide* (a base) gives *sodium chloride* (common salt) and water. *Metals*, too, react with acids, forming **salts.** Thus, zinc with hydrochloric acid gives zinc chloride (a *salt*) and hydrogen.

These reactions are shown in the equations, —

$$\underset{40}{NaOH} + \underset{36.5}{HCl} \longrightarrow \underset{58.5}{NaCl} + \underset{18}{H_2O}, \text{ and}$$

$$\underset{65}{Zn} + \underset{73}{2\ HCl} \longrightarrow \underset{136}{ZnCl_2} + \underset{2}{H_2}.$$

The properties of acids, bases, and salts will be considered in the next chapter.

Hydrochloric acid is one of the most important acids. It is made on a large scale, and is used in enormous quantities to prepare chlorine and chlorides.

96. Chlorides. — The *chlorides* may all be considered *hydrochloric acid with its hydrogen replaced by a metal;* the acid itself is often called **hydrogen chloride.** The most important chlorides have been given in § 80;

others are ***barium chloride***, $BaCl_2$, ***silver chloride***, AgCl, and *ferric chloride*, $FeCl_3$. The most abundant chloride is, of course, *common salt*, NaCl.

The chlorides of most of the common metals are soluble in water. Exceptions are *silver chloride*, AgCl, and *mercurous chloride*, HgCl. *Lead chloride*, $PbCl_2$, is only slightly soluble in *cold* water, but more readily in hot water.

When, therefore, solutions of salts of silver, lead, and mercury (in its mercur***ous*** condition) are treated with a solution of a chloride, the chlorides of these metals are *precipitated.*

97. Exercises.

1. 300 c.c. of hydrogen and 250 c.c. of chlorine were mixed and exploded. What was the product? Its volume? Which of the gases used was in excess? How much?
2. Calculate the percentage composition of hydrochloric acid?
3. How many grams of sodium chloride are needed to yield, with sulphuric acid, 20 grams hydrochloric acid gas?
4. How many grams hydrochloric acid can be made from 35 grams potassium chloride, KCl?
5. What weight of sodium chloride is necessary to produce, with sulphuric acid, 20 liters of hydrochloric acid gas when 1 liter of hydrochloric acid gas weighs 1.63 grams?

CHAPTER VIII.

ACIDS, BASES, AND SALTS.

98. **Acids.** — In all of our study of Chemistry we shall have to deal constantly with bodies belonging to the classes *acids*, *bases*, or *salts*. Let us first consider some of the acids. One of these, viz., *hydrochloric acid*, we have already studied at some length; other important acids are *nitric acid*, *sulphuric acid*, *acetic acid*, and *tartaric acid*. Only a short description of these will be given here.

Nitric acid, HNO_3, is a colorless liquid. It ordinarily has a sharp odor and is very corrosive in concentrated form. It turns the skin yellow. A dilute solution of nitric acid is sour, turns blue litmus and neutral litmus pink, decomposes carbonates, *e. g.*, marble, or calcium carbonate, and acts upon many metals.

Sulphuric acid, H_2SO_4, is a heavy, oily liquid which dissolves in water with the evolution of much heat. It chars organic substances, and therefore becomes dark colored when exposed for a time to the dust of the air. Its dilute solution has a sour taste, and acts upon litmus and carbonates as nitric and hydrochloric acids do. With many metals dilute sulphuric acid gives sulphates and hydrogen.

Acetic acid, $HC_2H_3O_2$, is a colorless, sharp-smelling liquid. Like the other acids, it has a sour taste, acts upon litmus, and decomposes carbonates. Vinegar is a dilute solution of acetic acid.

Tartaric acid, $H_2C_4H_4O_6$, is a white, crystalline solid, soluble in water. Its solution has properties similar to those of the other acids.

All of the acids named, except hydrochloric acid, may be looked upon as water joined to an oxide. The oxide is called the **anhydride** of the acid.

Thus nitrogen pentoxide, N_2O_5, is the *anhydride* of nitric acid, for

$$N_2O_5 + H_2O = 2\ HNO_3.$$

Similarly, sulphur trioxide, SO_3, is the anhydride of sulphuric acid.

The most important property of all acids is their power of reacting with the hydroxides of metals. When a solution of any of the above acids is treated with a solution of a metal hydroxide, *e. g.*, sodium hydroxide, an evolution of heat takes place, and if the correct amount of sodium hydroxide is used, the *taste* of the acid, its *power to change litmus*, and to act upon *carbonates* and *metals*, will all disappear. The acid has been **neutralized** by the sodium hydroxide.

99. Bases. — The general properties of sodium hydroxide and its relation to water have already been given (*cf.* § 46).

Sodium hydroxide, NaOH, is a white solid which attracts moisture and carbon dioxide from the air, and thus becomes converted into sodium carbonate. Its solution changes *pink* and neutral litmus *to blue*, feels *soapy* to the touch, and has a *bitter*, *alkaline* taste.

Potassium hydroxide, KOH, resembles sodium hydroxide closely. Its aqueous solution has properties *almost* identical with those of sodium hydroxide.

Ammonium hydroxide, NH_4OH, is not known in the free condition. Its aqueous solution smells strongly of *ammonia*, owing to the constant evolution of this gas, but its reaction to litmus, etc., is much like that of sodium and potassium hydroxides.

Calcium hydroxide, $Ca(OH)_2$, is a white solid made by adding the necessary amount of water to *quicklime*, CaO. Calcium hydroxide is slightly soluble in water; the solution is called *lime-water.*

Barium hydroxide, $Ba(OH)_2$, is much more soluble than calcium hydroxide. Its solution is called *baryta water.*

All of these hydroxides, and many more, are grouped together under the general name, *bases*. The most *active* bases are sodium and potassium hydroxides, which, with ammonium hydroxide, are called **alkalies.**

As has already been stated (*cf.* § 47), hydroxides may be looked upon as water with half of its hydrogen replaced by a metallic element. This is true of calcium hydroxide, having the formula $\mathrm{Ca}^{\mathrm{OH}}_{\mathrm{OH}}$, no less than of sodium hydroxide, $NaOH$. The formula $\mathrm{Ca}^{\mathrm{OH}}_{\mathrm{OH}}$, however, must be thought of as derived from 2 H_2O, or $\left\{\begin{matrix}\mathrm{H-OH}\\ \mathrm{H-OH}\end{matrix}\right.$. Similarly, the formula $\mathrm{Fe}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{OH}}}$ or

$Fe(OH)_3$, for ferric hydroxide, is derived from $\left\{\begin{matrix}HOH\\HOH\\HOH\end{matrix}\right.$ by replacing half of the hydrogen there represented by Fe.

100. Neutralization. — A comparison of the formulas of the hydroxides named will show that *they all contain the group OH* (called **hydroxyl**) taken one or more times. On the other hand, the formulas of the acids show that *the acids all contain hydrogen*, taken *once*, *twice*, etc., in each formula. Furthermore, the neutralization of acids by bases produces *salts* and *water*, as is shown by the following equations: —

$$NaOH + HCl = NaCl + H_2O.$$
$$KOH + HCl = KCl + H_2O.$$
$$2\ KOH + H_2SO_4 = K_2SO_4 + 2\ H_2O.$$
$$2\ NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2\ H_2O.$$
$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O.$$
$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2\ H_2O.$$
$$Ba(OH)_2 + 2\ HCl = BaCl_2 + 2\ H_2O.$$

The *neutralization of properties* which takes place when a basic hydroxide and an acid are brought together thus *consists in the union of the hydrogen of the acid with the hydroxyl of the base to form water.* The *metal* of the hydroxide and *all but the hydrogen* of the acid are found, on evaporation of the water, combined in the resulting *salt.*

The formula of an acid *minus* the replaceable hydrogen is called the **acid radical.**

101. The Action of Oxides with Acids. — The oxides of the metals, like the hydroxides, react with acids to form salts and water. Thus, the equation

$$CaO + 2\ HCl = CaCl_2 + H_2O$$

might represent the reaction between calcium oxide and hydrochloric acid, just as the equation

$$Ca(OH)_2 + 2\ HCl = CaCl_2 + 2\ H_2O$$

represents that between calcium hydroxide and the acid. The only difference is that the second equation shows twice as much water as the first. This is because the hydroxide is the oxide *plus* water.

It is probable, however, that the oxides of the metals react with acids only in the presence of water. If this is so, we must assume that it is the *hydroxide* that reacts, and not the oxide. The action of calcium oxide upon aqueous hydrochloric acid would, therefore, be represented thus: —

(1) $CaO + H_2O = Ca(OH)_2$.
(2) $Ca(OH)_2 + 2\ HCl = CaCl_2 + 2\ H_2O$.

For the same reason the action of sodium oxide upon sulphuric acid would be represented thus: —

(1) $Na_2O + H_2O = 2\ NaOH$.
(2) $2\ NaOH + H_2SO_4 = Na_2SO_4 + 2\ H_2O$.

102. Salts. — Salts may be looked upon as *acids in which hydrogen has been replaced by* **metals.** By no means *all* of the hydrogen of many acids is replaceable by metals, but when all that can be has been replaced, the resulting substance is called a *normal salt*. The normal

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salts formed by such strong acids as sulphuric acid, nitric acid, and hydrochloric acid with such electropositive metals as sodium, potassium, and the group ammonium, are *neutral* in their properties, *i. e.*, they will not turn blue litmus red, nor red, blue, but will produce in *sensitive* litmus a characteristic lavender color. The taste of such salts resembles that of common salt.

But a salt may be *normal* without being *neutral.* Thus, sodium carbonate is a normal salt, but the reaction of its solution toward litmus is that of a base. Ferric sulphate solution, on the contrary, has an acid reaction.

103. Acid Salts. — In many cases, the hydrogen of the acid is replaceable by metals in *two* or more stages (*cf.* § 92); hence *there may be two or more salts formed by the acid with the same basic hydroxide.* The following equations illustrate this: —

$$\begin{aligned}&NaOH + H_2SO_4 = NaHSO_4 + H_2O.\\&2\ NaOH + H_2SO_4 = Na_2SO_4 + 2\ H_2O.\\&KOH + H_2CO_3 = KHCO_3 + H_2O.\\&2\ KOH + H_2CO_3 = K_2CO_3 + 2\ H_2O.\end{aligned}$$

The substance $NaHSO_4$ is *sodium hydrogen sulphate,* while Na_2SO_4 is *sodium sulphate.* Similarly, $KHCO_3$ is *potassium hydrogen carbonate,* but K_2CO_3 is *potassium carbonate.*

The salts in which there is still replaceable hydrogen are called *acid salts.* Acid salts may usually be converted into normal salts by the addition of enough of the hydroxide to replace all the replaceable hydrogen, and, conversely, normal salts [illegible] acid salts by treatment with [illegible] —

$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O$$
$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O$$

So, also,
$$Na_2SO_4 + H_2SO_4 = 2NaHSO_4$$
$$Na_2CO_3 + H_2CO_3 = 2NaHCO_3$$

Solutions of acid salts have [illegible] toward litmus, but [illegible] sometimes be *alkaline* [illegible] drogen carbonate and [illegible] Na_2HPO_4.

104. Basic Salts. — A [illegible] two points of view, either [illegible] of which has been replaced [illegible] *droxide* with its hydroxyl (OH) [illegible] metallic element or by an [illegible] Thus sodium chloride, NaCl [illegible] hydrochloric acid, HCl, with hydrogen [illegible] dium, or as sodium hydroxide, NaOH, [illegible] replaced by chlorine. Similarly, [illegible] $CaCl_2$, is calcium hydroxide, $Ca(OH)_2$, [illegible] replaced by chlorine; and calcium sulphate, $CaSO_4$, is calcium hydroxide with hydroxyl replaced by the [illegible] radical SO_4. Now, just as in sulphuric acid, H_2SO_4, the hydrogen may be replaced half at a time, so in calcium hydroxide the hydroxyl groups may be substituted, *theoretically*, in *two* stages. We *might*, therefore, have from calcium hydroxide and hydrochloric acid two compounds, (1) $\mathrm{Ca}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{Cl}}$, and (2) $\mathrm{Ca}\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{Cl}}$. Just as we call a salt which still contains replaceable hydrogen an *acid* salt, so we call one having replaceable hydroxyl groups a *basic salt.*

To illustrate: Just as *phosphoric acid,* H_3PO_4, may have *two acid sodium salts,* viz., NaH_2PO_4 and Na_2HPO_4, so *bismuth hydroxide,* $Bi(OH)_3$, might have *two basic nitrates,* viz., $\mathrm{Bi}\genfrac{}{}{0pt}{}{(\mathrm{OH})_2}{\mathrm{NO}_3}$ and $\mathrm{Bi}\genfrac{}{}{0pt}{}{\mathrm{OH}}{(\mathrm{NO}_3)_2}$. The normal nitrate is, of course, $Bi(NO_3)_3$.

It is to be noted, however, that some basic salts have, apparently, a more complex constitution.

105. Basicity and Acidity. — The number of stages in which the replaceable hydrogen of an acid can be substituted by metals determines the **basicity** of the acid. Thus, hydrochloric acid, HCl, nitric acid, HNO_3, and acetic acid, $HC_2H_3O_2$, are *monobasic* acids; carbonic acid, H_2CO_3, and sulphuric acid, H_2SO_4, are *dibasic;* while phosphoric acid, H_3PO_4, is *tribasic.*

In the same way, the number of stages in which the hydroxyl groups of a basic hydroxide might be replaced by acid radicals or by non-metals determines, roughly, the *acidity* of the hydroxide. Thus sodium hydroxide and potassium hydroxide are *monacidic* bases; calcium hydroxide, $Ca(OH)_2$, and barium hydroxide, $Ba(OH)_2$, are *diacidic;* while bismuth hydroxide, $Bi(OH)_3$, is *triacidic.*

106. Nomenclature of Acids. — Acids consisting of hydrogen and an electro-negative element, *e. g.*, hydrochloric acid, HCl, are designated by the names of *both* elements. Thus HBr is *hydrobromic* acid, and H_2S is *hydrosulphuric* acid.

Such compounds are often named like ordinary compounds of two elements (*cf.* § 77); thus: hydrogen chloride, hydrogen sulphide, etc.

The salts of such acids are called chlorides, bromides, sulphides, etc. Thus, the sodium salt of hydriodic acid is called ***sodium iodide***, and the barium salt of hydrochloric acid is ***barium chloride.***

Most acids, however, consist of a *non-metallic element united with hydrogen and oxygen*, e. g., nitric acid, sulphuric acid, phosphoric acid, acetic acid, etc.; these are given the name of the non-metallic element with the final syllable **ic**. This method of nomenclature applies, however, only to *inorganic* acids; *organic* acids, *e. g.*, acetic, tartaric, citric, picric, etc., acids are quite arbitrarily named.

When there are two acids containing the same three elements in different proportions, the ending of the acid containing the greater proportion of the *non-metallic* element is made **ous**, while the ending of the one containing less of this element is made **ic**. Thus, nitrogen forms with hydrogen and oxygen at least two compounds which are acids; of these the one containing the more nitrogen — its formula is HNO_2 — is called *nitrous* acid, while the one containing the smaller proportion of nitrogen is called *nitric* acid. So sulphur forms with hydrogen and oxygen both *sulphurous* acid, H_2SO_3, and *sulphuric* acid, H_2SO_4.

The acids formed by the element chlorine, however, give the best illustrations of nomenclature. Chlorine forms with hydrogen and oxygen *four* acid compounds, the compositions of which are represented by the formulas :—

$$\begin{gathered} HClO, \\ HClO_2, \\ HClO_3, \\ HClO_4. \end{gathered}$$

The second of these compounds, $HClO_2$, is called *chlorous* acid ; the third, *chloric* acid ; the first, because it contains less oxygen than chlorous acid, is called *hypochlorous* acid (" **hypo** " signifies " under " or " lower than ") ; the fourth, because it has more oxygen than chloric acid, is called *perchloric* acid.

Acids containing a non-metallic element united with hydrogen and oxygen are called *oxygen acids.*

107. Nomenclature of Salts. — The salt of an acid ending in *ous* is given the ending **ite,** the prefix *hypo* remaining unaltered, if present.

Thus, the sodium salt of nitrous acid is sodium *nitrite*, $NaNO_2$; the potassium salt of chlorous acid is potassium *chlorite*, $KClO_2$; and the calcium salt of hypochlorous acid is calcium *hypochlorite*, $Ca(OCl)_2$.

The salt of an acid ending in *ic* is given the suffix **ate,** the prefix *per* remaining unchanged, if present.

Thus, the ammonium salt of nitric acid is ammonium *nitrate*; the barium salt of chloric acid is barium *chlorate*, $Ba(ClO_3)_2$; the potassium salt of permanganic acid is potassium *permanganate*, $KMnO_4$.

In many cases there are two salts of the same metal with a given acid, as, for example, two iron sulphates, designated by the formulas $FeSO_4$ and $Fe_2(SO_4)_3$, respectively. To distinguish between these the ending of the name of the metal is changed to **ous** in the case of the sulphate having the greater proportion of the metal, and to **ic** in the case of the compound having the smaller proportion of the metal.

Thus, $FeSO_4$ is called *ferrous* sulphate, just as $FeCl_2$ is called *ferrous* chloride (*cf.* § 78); and $Fe_2(SO_4)_3$ is called *ferric* sulphate, just as $FeCl_3$ is called *ferric* chloride.

108. Nomenclature of Bases. — The name of a basic hydroxide contains the names of all the elements of which the hydroxide is composed. The ending is **ide**, the radical **OH** being treated as an element. When there are two basic compounds of *hydroxyl* with the same metal, the name of the metal in the hydroxide having the larger proportion of the metal ends in **ous**, while the ending of the metal in the other hydroxide is **ic**.

Thus, we have *cuprous hydroxide*, $Cu_2(OH)_2$, and *cupric hydroxide*, $Cu(OH)_2$; also *ferrous hydroxide*, $Fe(OH)_2$, and *ferric hydroxide*, $Fe(OH)_3$.

The oxygen of air is removed more satisfactorily by hot copper. The apparatus is shown in Fig. 26.

Purer nitrogen may be prepared by heating *ammonium nitrite*, NH_4NO_2. The reaction takes place as shown by the equation, –

$$\underset{64}{NH_4NO_2} = \underset{28}{N_2} + \underset{36}{2\,H_2O}.$$

Instead of ammonium nitrite, a mixture of solutions of ammonium chloride (NH_4Cl) and sodium nitrite ($NaNO_2$) is generally used. When this mixture is heated carefully, a regular stream of nitrogen is evolved.

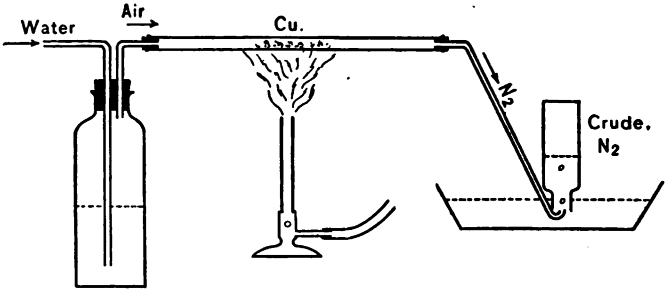


FIG. 26.

112. **Properties of Nitrogen.** — Pure nitrogen is a gas without taste, odor, or color, and about 0.97 as heavy as air. 100 c.c. of water under ordinary conditions can dissolve only about 1 c.c. of the gas. *One*

liter of nitrogen weighs about 1.25 grams *at standard conditions*, i. e., at 0° C. and 760 mm. pressure.

Since ordinary combustion and respiration require oxygen, it naturally follows that "atmospheric nitrogen," *i. e.*, air deprived of oxygen, no longer supports either combustion or respiration. Pure nitrogen, like atmospheric nitrogen, is an extremely inactive substance, combining directly with only a few elements. It does combine with magnesium, titanium, lithium, etc., at an elevated temperature, giving **nitrides.**

Under the influence of the electric spark, nitrogen unites with hydrogen and oxygen to form nitrous and nitric acids, and with hydrogen alone to form ammonia; hence these compounds, and the substances formed from them, viz., *ammonium nitrite* and *ammonium nitrate*, are found in the atmosphere, in natural waters, and in the soil.

113. "Atmospheric Nitrogen" a Mixture. — The nitrogen obtained by removing oxygen from air was long considered pure, but careful experiment made the weight of a liter of atmospheric nitrogen 1.2571 grams and that of a liter of pure nitrogen 1.2507 grams. The cause of this difference was investigated and found to be due to the fact that atmospheric nitrogen contains another substance heavier than nitrogen. Thus *argon* was discovered in 1894.

114. Character of the Atmosphere. — The atmosphere is the gaseous mantle of the earth. Some of its ingredients are practically *constant* in amount, but others are *variable.*

Constant Ingredients.

Nitrogen,
Oxygen,
Argon,
Helium,
Hydrogen,
and several rare
and recently discovered
substances.

Variable Ingredients.

Water,
Carbon dioxide,
Ozone,
Hydrogen peroxide,
Ammonium nitrite,
Dust,
etc.

Bacteria are so universally present and of such great importance to many changes taking place in the atmosphere that they may rightly be classed among its variable ingredients.

By *pure* air we mean a mixture of the constant constituents of the atmosphere. The proportions, by volume and by weight, of the three most abundant of these are as follows: —

	BY VOLUME.	BY WEIGHT.
Nitrogen,	78.06%	75.5%
Oxygen,	21.00%	23.2%
Argon,	0.94%	1.3%

Hydrogen exists in small quantities in the atmosphere. Recent experiments with the air of Paris show that 100 liters of it contain about 19 c.c. of hydrogen. Hydrogen is thus present in almost as great an amount by volume as carbon dioxide (*cf.* § 117).

Nitrogen and oxygen, the most abundant constituents of air, have been described already. Argon and helium, while not at all comparable with the former two elements in importance, are interesting because they have only recently been discovered in the earth; hence a short description of each follows.

115. Argon. — The discovery of argon *almost* took place a hundred years before this substance was actually studied by Ramsay and Rayleigh in 1894; for Cavendish, the discoverer of hydrogen, records the observation that he could not get all the nitrogen of the air to combine with oxygen by "sparking" a mixture of these gases in the presence of potassium hydroxide. This was in 1785. The "residual nitrogen" was argon and the other inert gases which are mixed with atmospheric nitrogen. By repeating Cavendish's experiments, Ramsay and Rayleigh obtained argon.

A second way of obtaining this substance is to pass pure air over heated copper, which takes up the oxygen, and then over magnesium, which absorbs the nitrogen as *magnesium nitride*, Mg_3N_2. The nitrogen may also be removed by lithium or calcium.

Argon may be condensed to a colorless liquid, boiling at —185° C., and at lower temperatures may even be obtained in the solid state. In gaseous form it is heavier than oxygen. It is much more soluble in water than nitrogen, hence in air which has been dissolved in water and afterward expelled from solution, the proportion of argon is greater than in the atmosphere. Argon is *almost without chemical activity*, hence its name.

116. Helium. — By means of the spectroscope, helium was discovered to be a constituent of the sun a quarter of a century before it was known to exist on the earth.

It has been found in small amount in the earth's atmosphere, in certain rare minerals, in some springs, and in a meteorite, as well as in the atmospheres of the sun and certain fixed stars. Like argon, helium is very inert. *It is probably less soluble in water than any other gas.*

117. Carbon Dioxide in the Atmosphere. — The chief *variable* constituents of the atmosphere are carbon dioxide and steam, and to the presence of these two substances many of the properties of the atmosphere are due. The atmosphere supports the life of chlorophyll-producing plants largely because it contains carbon dioxide.

The presence of carbon dioxide in the atmosphere may be shown by drawing a current of ordinary air through a solution of calcium hydroxide (lime-water); the white solid which separates from solution is calcium carbonate, $CaCO_3$. Its formation indicates the presence of carbon dioxide in the air.

Under ordinary conditions, 10,000 parts, by volume, of air contain only 3 or 4 parts of carbon dioxide. If this relative amount of the gas is doubled as a result of respiration, the air becomes foul, not so much because of the carbon dioxide itself as because of the decaying organic matter which is exhaled along with it from the lungs of animals. The quantity of carbon dioxide in the atmosphere of a room thus serves as an *index* to the amount of poisonous material present.

The great weight of the earth's atmosphere may be illustrated by the fact that its carbon dioxide, although so small a proportion of the whole, is estimated to weigh over five thousand billions of tons.

118. Water Vapor in the Atmosphere. — The quantity of water vapor which the atmosphere is capable of holding at any given time depends upon the temperature and the pressure. *Air is saturated with water vapor*, or at the "*dew-point*," when the *slightest reduction* of temperature or *increase* of pressure causes *precipitation* of some of the water.

One hundred liters of air at 25° C. and at ordinary pressures can hold a little over 2 grams of water. If the temperature falls to 0° C., about 1.7 grams of the water are precipitated as rain. Usually the atmosphere is far from having all the water it can hold, only 60%, or less, of this amount being present on a fair day. If there is much more than this, we recognize its presence by the "closeness" of the atmosphere.

119. Atmospheric Dust. — The importance of atmospheric dust in causing certain phenomena is well known. It causes sunset and sunrise colors, and helps to effect the precipitation of water vapor as clouds and rain. An experiment to illustrate the latter influence is the following: —

A large flask (Fig. 27) is filled with dust-free air by drawing through it, for some hours, air which has passed through a long tube of cotton wool. If the room is now darkened, and a beam of light is directed through a small opening toward the flask, the beam will be visible in the outer air, but not in the flask, owing to the absence of dust. A small amount of steam is next introduced into the flask by connecting the flask at *a* with a vessel of boiling water, opening the pinch clamps at *a* and *b*, and sucking for a moment with the aspirator. A beam of light, directed as before, will be practically invisible. The beam will still be invisible when the flask is connected with the aspirator and partly exhausted. A small funnel is now attached to the tube at *a*, and a quantity of smoke is produced in the mouth of the funnel. This smoke is sucked into the large flask by opening the clamps at *a* and *b*, and thus making connection with the aspirator. If now the clamp *a* is closed, and the air is slightly exhausted through *b*, a beam of light passing through the flask will be clearly visible owing to the small drops of water, *i. e.*, mist, which fill the flask. In a similar way the dust of the air probably causes the formation of *drops* of water.

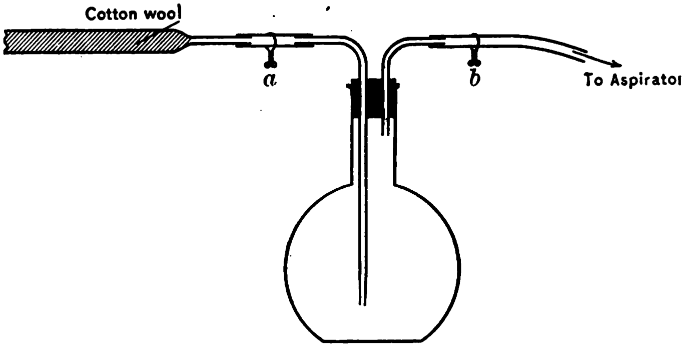


FIG. 27.

120. Weight and Pressure of the Atmosphere. —

One liter of air weighs, at standard temperature and pressure, 1.293 grams, and is, therefore, $\frac{1}{773}$ as heavy as water, and about 14.4 times as heavy as hydrogen. Because of its weight, the atmosphere exerts pressure upon all bodies immersed in it. This pressure is measured by the height of the column of mercury the atmosphere will support in the barometer (Fig. 28). The mean height of the barometer at 0° C. and at sea level is 760 mm.; this is the *standard* barometric height, and is called a pressure of *one atmosphere.*

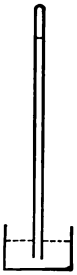


FIG. 28.

A column of mercury 760 mm. high and 1 sq. cm. in cross sectional area weighs 1,033.6 grams; hence this is the pressure of the atmosphere upon 1 sq. cm. at sea level. If the liquid used is water, which is $\frac{10}{136}$ as heavy as mercury, the height of the barometer will be *13.6 times as great* as with mercury, *i. e.*, 10.4 meters, or 34 feet.

121. Liquefaction of Air. — The condensation of air to the liquid condition is brought about by the same methods as those used to liquefy other "permanent" gases, and differs radically from the liquefaction of gases like ammonia, chlorine, and sulphur dioxide. These gases may be condensed *at ordinary temperatures*, if only sufficient pressure is applied; but gases like air cannot be liquefied at the ordinary temperature *by any pressure, however great.* Indeed, pressures up to 3,600 atmospheres have been applied without avail. This is due to the fact that there is for every gaseous substance a maximum temperature above which the gas *cannot* be liquefied; this is called the **critical** temperature of the gas.

A "*permanent*" gas thus differs from an easily condensible gas in this respect, viz., that the critical temperature of a condensible gas is *above* the ordinary temperature, while that of the permanent gas lies far *below* the ordinary temperature. Such gases as air, hydrogen, etc., are, therefore, condensed only at a very low temperature and great pressure.

Two general methods are used to liquefy true gases. In the *first* method the gas to be condensed is first cooled to its critical temperature, and is then subjected to pressure. In the *second* method the gas is first strongly compressed, and is then cooled to its critical temperature.

The second method has been used recently to liquefy air on a commercial scale.

The apparatus used consists, essentially, of two systems of pipes, the pipes of the outer system forming a jacket surrounding those of the inner system. The air of the inner system is that to be liquefied.

By means of compressing engines (*cf.* Fig. 34), air is forced into each system under great pressure. Much heat is thereby evolved. *When the compressed air has cooled* to the ordinary temperature, some of the air of the outer pipes is allowed to escape. *The sudden expansion* of the air remaining in the *outer* pipes then causes an amount of heat to be absorbed which is equal to that evolved when the compression took place. The air of the outer pipes, *now intensely cold*, cools the compressed air of the inner pipes below the critical temperature of air, and thus liquefies it.

122. Properties of Liquid Air. — In the liquid condition air is colorless, has about the same density as water, and boils at —190° C., under ordinary pressure. When freshly made, liquid air is about half oxygen, but the proportion of oxygen increases by the evaporation of the nitrogen (liquid nitrogen boils about 10° C. below liquid oxygen) until the liquid is over 90% oxygen.

Liquid air is preserved in open, double-walled vessels called *Dewar bulbs* (Fig. 29). The space between the walls of the bulbs is exhausted of air to secure non-conductivity of heat. Tin or wooden boxes having double walls filled with silk may also be used.

Alcohol, liquid carbon dioxide, mercury, etc., solidify when placed in liquid air, and steel burns in it like tinder; yet the hand may be held in it for a short time without injury, because protected by a non-conducting film of air in the gaseous state.

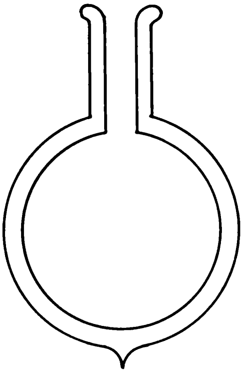


FIG. 29.

123. Determination of the Proportion of Oxygen in Air. — The amount of oxygen in a given volume of air is usually determined either (1) by absorbing the oxygen, or (2) by exploding the air with a known volume of hydrogen.

The *phosphorus absorption method*, a crude form of which was described under nitrogen (*cf.* § 111), is carried out more accurately as follows: —

A gas analysis tube, partly full of air, is inverted in a hydrometer jar (Fig. 30), and the gas volume is carefully measured. The temperature and pressure are recorded. A thin stick of phosphorus is introduced into the tube by means of a bent wire, and is left there twenty-four hours. The phosphorus is then removed, and the residual gas is measured. When the necessary corrections have been made, the volume of oxygen absorbed by the phosphorus and, consequently, the per cent of oxygen in the original air are readily calculated.

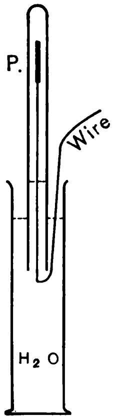


FIG. 30.

The absorption of the oxygen by potassium pyrogallate gives similar results.

The second general method, viz., the explosion of a mixture of known volumes of air and hydrogen, may be illustrated as follows: —

In the straight eudiometer tube shown in Fig. 31, a known volume of air is mixed with an excess of hydrogen, and the electric spark is passed through the mixture. All of the oxygen of the air taken will thus unite with hydrogen to form water. The volume of *steam* formed

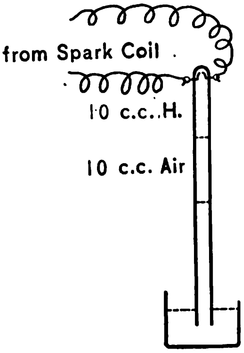


FIG. 31.

will be equal to that of the hydrogen used up, but the volume of *liquid* water produced by the condensation of the steam will be insignificant. Hence there will be a *contraction* of volume. One-third of this contraction will be the volume of oxygen present in the original air.

To take a concrete example: If 10 c.c. of each of the gases, air and hydrogen, are taken, the volume remaining after the explosion will be about 13.7 c.c., *i.e.*, the contraction will be 6.3 c.c. Of this contraction 2.1 c.c. (= ⅓ of 6.3) are oxygen; hence 10 c.c. of air contain 2.1 c.c. (= 21%) of oxygen.

The proportions of the chief *constant* constituents of the atmosphere have been determined in many different places, and have been found everywhere practically the same. This is a remarkable fact when we remember that air is only a physical mixture, yet it is a necessary consequence of the circulation of the air and the rapid diffusion of its gases.

124. The Air a Physical Mixture. — That air is not a *compound* of nitrogen and oxygen is proved by several facts, of which the following are illustrations: —

(1) When nitrogen and oxygen are mixed, there is no evidence of union, such as evolution or absorption of heat, change of volume, etc.

(2) If air were a chemical compound, like the nitrogen oxides, it ought to have the same composition in the liquid state as in the gaseous. This, however, is not the case, as was stated in the description of liquid air.

(3) There is no reason why air, if a compound, should

have its composition changed by solution in water; yet this is the case. Air that has been expelled from solution in water contains about 35%, by weight, of oxygen, instead of 23%, owing to the fact that oxygen is much more soluble than nitrogen.

125. Exercises.

1. Calculate the composition, in parts per cent, of a mixture of gases 76 c.c. of which contain 48 c.c. oxygen, 12.5 c.c. hydrogen, and the remainder nitrogen.

2. It has been calculated that in certain places 900 grams of nitric acid fall every year upon an acre of ground; can you suggest how it is formed?

3. Why is not all the carbon dioxide of the air at or near the earth's surface?

4. What is the height, in inches, of a barometer standing at 742 mm.? (See Appendix.)

5. 16 c.c. of a mixture of nitrogen and oxygen were put with 25 c.c. pure hydrogen, and exploded. The volume of residual gas was 23 c.c. How many cubic centimeters of the original mixture were oxygen?

6. How many grams of nitrogen can be obtained by decomposing 16 grams of ammonium nitrite? How many liters at standard conditions?

7. How many liters of "atmospheric nitrogen" can be obtained from 10 liters of air? What will be its weight at standard conditions?

CHAPTER X.

PROPERTIES OF GASES. THE MOLECULAR THEORY.

126. Gases and Vapors. — The word "**gas**" is often used to denote a substance which is in the gaseous state under ordinary conditions, while "**vapor**" is used to mean the gaseous condition of a substance which is ordinarily liquid or solid. Thus, we speak of oxygen as a *gas*, but of steam as the *vapor* of water. In reality, however, the term "gas" can properly be applied only to a gaseous body *above its critical temperature*. In this sense, chlorine and hydrochloric acid are not gases under ordinary conditions, while nitrogen and hydrogen are. Boyle's and Charles' laws, which follow, are applicable *in a strict sense* only to true gases. They are, however, *approximately* true for all gaseous bodies at moderate pressures.

127. Relation of the Volume of a Gas to Pressure. — *At a constant temperature the volume of a gas is inversely proportional to the pressure* the gas supports. This is **Boyle's law.** A mass of gas having a volume of 30 c.c. at 700 mm. thus occupies 27.63 c.c. at 760 mm. pressure, and 35 c.c. at 600 mm. pressure, as is evident from a solution of the proportions, —

$$30 : x :: 760 : 700, \text{ and}$$
$$30 : x :: 600 : 700.$$

The product of the number representing the volume of a gas and the number representing the pressure under which the volume is measured is, therefore, a constant; or,

$$v \times p = constant.$$

Since increasing the pressure will *diminish* the volume of a gas, it will plainly *increase* the mass of gas in a given volume, i. e., *the density*. Hence Boyle's, or, as it is sometimes called, **Mariotte's** law may be stated thus: *The density of a gas at constant temperature is proportional to the pressure.*

Problems involving changes of pressure may be solved as follows: —

Problem 1. A quantity of gas measures 120 c.c. when the pressure, as indicated by the barometer, is 720 mm.; what will its volume be at 760 mm.?

Solution. Since the volume varies inversely as the pressure, 120 c.c. in changing from a lower to a greater pressure must *diminish* in volume. Hence the proportion, $120 : x :: 760 : 720$. Whence $x =$ the volume at 760 mm.

Problem 2. What will be the volume at 650 mm. of a quantity of nitrogen which at 820 mm. has a volume of 50 c.c.?

Solution. Fifty c.c. in changing from a pressure of 820 mm. to one of 650 mm. must *increase* in volume. Hence the proportion, $50 : x :: 650 : 820$.

128. Relation of Volume to Temperature. — The pressure remaining constant, a change of **temperature**

alters the volume of a gas so that 273 c.c. at 0° C. become 274 c.c. at 1° C., 283 c.c. at 10° C., 303 c.c. at 30° C., 253 c.c. at —20° C., etc. The reverse changes are also true, *i. e.*, 253 c.c. at —20° C. become 273 c.c. at 0° C.; and 303 c.c. at 30° C. become 283 c.c. at 10° C. and 273 c.c. at 0° C. These changes correspond to an increase of $\frac{1}{273}$ (= 0.00366) of the gas volume at 0° C. for every degree the temperature is raised above 0° C., and a like diminution for every degree the temperature of the gas falls below 0° C. *At —273° C.*, therefore, *the volumes of all gases would be 0.* This temperature (—273° C.) is called the *absolute zero.* All *centigrade readings may be changed to absolute readings by adding 273* to them. Thus, +10° C. = 283° abs. C., and —15° C. = 258° abs. C. The law expressing the relation of volume to temperature (Charles' law) may, therefore, be stated thus: *Under constant pressure the volume of a gas is proportional to its absolute temperature.*

It follows that the *pressure* exerted by a gas whose volume is kept constant *is proportional to the absolute temperature* of the gas.

Problems involving changes of temperature are solved as follows: —

Problem 1. Suppose that the temperature of a gas measuring 80 c.c. at 0° C. is changed to 20° C.; what volume will the gas have at 20° C.?

Solution. Since 273 c.c. at 0° C. become 293 c.c. at 20° C., 80 c.c. will *increase* a proportional amount. Therefore we write the proportion, 80 : x :: 273 : 293. Whence x = the required volume.

Problem 2. If 60 c.c. of oxygen at 30° C. have the temperature lowered to —10° C., what will the volume become?

Solution. Since 303 c.c. of a gas at 30° C. become 263 c.c. at —10° C., 60 c.c. of oxygen will *diminish* proportionally. Therefore, 60 : x :: 303 : 263.

129. Reduction to Standard Temperature and Pressure. — In § 123 we learned that the oxygen of an enclosed portion of air will be completely removed by phosphorus. From the volume of air taken and the volume of residual gas obtained the proportion of oxygen may be calculated. Accurate results cannot, however, be expected from this experiment unless the original and final volumes are *comparable*, i. e., are at the same temperature and pressure. It is *possible* that conditions will be the same after twenty-four hours; *probably*, however, the barometric reading and the temperature will have changed, and it will be necessary to reduce the volumes read to the same temperature and pressure for comparison. *The volumes of gases are usually compared* **at standard temperature and pressure,** *i. e.*, at 0° C. and 760 mm., respectively.

Problems of this kind, involving changes in both temperature and pressure, are solved by stating the proportion for each case, and then combining the two proportions.

Problem 1. What will be the volume, under standard conditions, of 40 c.c. of oxygen measured at 700 mm. and 25° C.?

Solution. (*a*) For the temperature-change alone, —

Since 298 c.c. (273 + 25) at 25° C. become 273 c.c. at 0° C., 40 c.c. will *diminish* proportionally. Therefore,

$$40 : x :: 298 : 273.$$

(*b*) For the change in pressure, —

Since the pressure is to *increase* from 700 mm. to 760 mm., the volume will be *diminished*. Hence the proportion,

$$40 : x :: 760 : 700.$$

Combining the two proportions, we have

$$40 : x :: \begin{matrix} 298 : 273; \\ 760 : 700; \end{matrix} \text{ or,}$$

$$298 \times 760x = 40 \times 273 \times 700.$$

Whence $x =$ the volume which 40 c.c. measured at 25° C. and 700 mm. would occupy at 0° C. and 760 mm.

Problem 2. In the experiment referred to in § 104, viz., the analysis of air by phosphorus, a student obtained the following figures : —

Volume of air taken for analysis = 45.6 c.c.
Temperature = 19° C.
Barometer reading (corrected) = 730 mm.

On the next day the figures were, —

Volume of residual gas = 35.7 c.c.
Temperature = 21° C.
Barometer reading = 742 mm.

Required the volume, per cent, of oxygen absorbed.

Solution. We first reduce the volume of air taken to standard conditions by solving for x in the proportion, —

$$45.6 : x :: \begin{matrix} 292 : 273. \\ 760 : 730. \end{matrix}$$

This done, we get the volume of the residual gas at standard conditions by solving for x in the proportion, —

$$35.7 : x :: \begin{matrix} 294 : 273. \\ 760 : 742. \end{matrix}$$

In this way we obtain comparable volumes. The per cent of oxygen in the air taken may now be found by solving for x in the equation, —

$$\frac{\text{Vol. of air} - \text{Vol. of residual gas}}{\text{Vol. of air}} = x.$$

130. Correction of the Barometric Reading.

— *The standard height of the barometer is 760 mm. at 0° C.;* at other temperatures the reading must be *corrected for temperature.* Thus at 20° C. the mercury column is 3 mm. longer than at 0° C.; hence this amount must be subtracted from the barometric reading at 20° C. to give the reading at 0° C.

Another correction is often made *when gases are measured over liquids*, viz., a correction for the *tension*, i. e., *pressure*, of the *vapor* of the liquids (*cf.* § 44). The pressure of this vapor *opposes* the atmospheric pressure, hence *the volume of a gas read over a liquid is greater than it would be if the gas were free from the vapor* of the liquid, *i. e.*, **dry**. To get the volume which a moist gas would have if dry, we must assume the gas to be, not at the pressure read from the barometer, but at the barometric pressure *minus* the pressure of the vapor of the liquid.

A table of the tension of the vapor of water at several temperatures appears in the **Appendix**.

The correction for the tension of aqueous vapor is not applied when two gas volumes which are to be compared (*cf.*

§ 129, Prob. 2) are both measured over water at approximately the same temperature (in which case the aqueous tensions are, evidently, equal), nor on a very "close" day, when the atmosphere itself is nearly at its dew-point.

131. The Molecular Theory. — The physical behavior of gases, as well as that of liquids and solids, and the laws which govern chemical action are best explained by the assumption that matter consists of **particles,** or **molecules.** Molecules are assumed to be separated from one another by distances which are *very small,* but which are yet, especially in the case of gases, very great as compared with the size of the molecules themselves. When we speak of *distances between molecules* we mean *average* distances; for molecules are not at rest, but, on the contrary, *in constant motion.* The *cause* of the motion of molecules is their own *inherent energy.* The *direction* of their motion is *along straight lines* except as the molecules collide with one another or with the walls of the containing vessel.

Because of frequent collisions, the energy of one particle of matter is probably not the same as that of other particles in the mass. When we measure the *degree* of heat, *i.e.,* the *temperature* of the mass, we get only the *mean* temperature of the particles in the neighborhood of the thermometer. There may be many particles far above the mean temperature, as well as many far below it.

The above is a short outline of the "**Molecular Theory.**" The student must remember that the existence of molecules is *assumed*, and that the simple explanation of phenomena which this assumption permits cannot have the same force as the phenomena themselves. Yet so necessary does this explanation seem at the present time that scientific men everywhere hold it.

132. The Physical States of Matter. — The theory of the existence of molecules explains the behavior of matter in its *three physical states* of **gas, liquid,** and **solid.**

When a substance is in the *gaseous* state, the energy of its particles is so great that the gas tends to fill any space presented to it, however great. Hence a gas confined in a vessel exerts *pressure* upon the walls of the vessel.

In the *liquid* state the energy of the particles is less than in the gaseous condition. At the same time, there is still great freedom of motion of the particles among themselves, so that a liquid takes the form of the vessel containing it.

When a substance is in the *solid* condition, its molecules are not ordinarily at liberty to alter their relative positions. As a result, a solid has a *definite form.*

133. Avogadro's Hypothesis. — Another assumption regarding molecules is of great importance, viz., that *in equal volumes of all* **gaseous** *substances, at the same temperature and pressure, there is practically the same number of molecules.*

This is the hypothesis enunciated by **Avogadro, an Italian** physicist, in 1811, and by Ampère in 1814. It was originally assumed to explain the similarity in the physical properties of all gases, and now seems so *probable* that it serves as a basis of chemical reasoning. Only by some such assumption can the laws of Boyle and of Charles be explained in a reasonable way.

134. Explanation of Diffusion. — Having in mind the molecular, or particle, theory of matter, we are able to explain many common phenomena in an intelligent manner. At the present time we shall confine ourselves to *diffusion*, or *solution* (*cf.* § 55).

In the case of *gases*, diffusion takes place *to an unlimited extent*, because the molecules are so far apart that there is practically no resistance to the passage of other particles between them.

An illustration is the mixing of the gases composing the air.

In the case of *liquids*, however, there is considerable resistance to diffusion, hence the amount of diffusion is usually *limited*. Thus, when ether and water are mixed, ether dissolves in water, and water in ether, up to a certain limit.

Solids diffuse into other solids very slowly, and then only *under great pressure*. An interesting case of solid diffusion is the formation of the alloy *solder* from its constituents *without melting*.

In Spring's experiments, lead and tin were subjected to a pressure of about six thousand atmospheres in steel molds. Under these conditions the solids *diffused into each other*, as gases do at ordinary pressure. The solder thus made has the same properties as that obtained by fusion.

135. Diffusion of Gases and of Liquids. — When layers of gases are brought over each other, the gases do not *permanently* adjust themselves according to their relative densities, but *mix* with each other until any given volume of the mixture contains the same amount of each gas as every other equal volume. Thus, if a jar of hydrogen is placed, mouth downward, over a jar of carbon dioxide turned mouth upward, and the junction between the jars is made *close*, some of the carbon dioxide will *ascend, against gravity*, into the upper jar, and some of the hydrogen will *descend* into the lower one.

This is due to the fact that the particles of carbon dioxide having the greatest energy detach themselves from the layer of this gas and enter that of the hydrogen. In the same way, those particles of hydrogen which have the greatest energy leave their proper layer and enter that of the carbon dioxide. Thus a mixture is formed, first at the plane of contact between the two layers, but gradually extending through the whole mass of the gases.

There is no reason to suppose that diffusion *ever* ceases in such a mixture.

The *rate* at which diffusion takes place is very different in the case of different pairs of gases. This may be illustrated by the diffusion of *bromine* vapor in air and in hydrogen. If a drop of bromine is placed in each of two small watch glasses, and one watch glass is covered with a tall jar of hydrogen and the other with a jar of air, bromine will rise in both, *against gravity*, but much more rapidly in one than in the other.

Diffusion takes place in the same way between two liquids, and between solvents and solutions, but it is slower in these cases than with gases.

136. Solution of Gases in Liquids. — When a layer of a gas is brought over a liquid, *e.g.*, air over water, *gas particles dissolve* in the liquid, and, on the other hand, gas particles that were dissolved *leave* the liquid, until a condition of *equilibrium* is reached at which as many gas particles enter the liquid in a given time as leave it in the same time.

Similarly, the energy of some of the particles of the liquid causes them to leave the liquid surface, and to enter the gas above, until as many particles of the vapor of the liquid return to the liquid in a given time as leave it in the same time.

If the gas layer above the liquid is *in motion*, as when a current of air passes over water, this condition of equilibrium is never reached; hence the water *evaporates.*

The explanation of *efflorescence* and *deliquescence* (*cf.* § 53) is found here. The efflorescence of a solid is due to the fact that the crystal-water of the solid has a *greater* vapor tension (*cf.* §§ 44 and 130) than that of the water of the atmosphere. *Deliquescence*, on the contrary, is due to the fact that the water which the deliquescent substance has absorbed from the air has a *smaller* vapor pressure than that of the water of the air Hence moisture is added to the substance.

137. Solution of Solids in Liquids. — A solid dissolves in a liquid as a gas does. The energy of the particles of the solid causes them to leave the surface of the solid and to enter the solvent. At the same time there is a constant *return* of particles that have dissolved, to the *solid* state. These two operations go on until there are as many dissolved particles becoming solid in a given time as there are solid particles being dissolved in the same time.

When this condition of equilibrium has been reached, the solution is *saturated*, not because no further diffusion between solid and liquid goes on, but because further action cannot affect either the mass of undissolved solid or the concentration of the solution.

The gradual solution of a solid may be illustrated by putting some solid potassium permanganate, $KMnO_4$, into a deep bottle of water and leaving the vessel covered and undisturbed for some time.

Since, in the solution of a solid in a liquid, *the particles that get away from the solid are those having the greatest energy*, the addition of heat should *aid* solution by giving more particles sufficient energy to enable them to leave the solid. This is the case; for the solubility of most solids *increases with rise of temperature.* If the heat required is not furnished from an outside source, it comes from the solvent. Hence the dissolving of solids usually causes a *reduction of temperature.*

138. Osmotic Pressure. — We can observe and measure the tendency of the particles of a dissolved substance to diffuse through a solution by *preventing* the diffusion. To do this, we use a cell which permits the solvent to pass through its pores, but does not allow the dissolved substance to get through. *Such a cell is said to be* **semi-permeable.** The pellicles of most organic cells, many animal membranes, and certain inorganic substances, *e. g.*, copper ferrocyanide, have this property of semi-permeability.

To illustrate: If a solution of sugar in water fills a semi-permeable cell, and the cell is attached by a water-tight joint to a long glass tube and then immersed in pure water, there will be a very noticeable rise of the solution in the glass tube. The height to which the liquid in the tube rises above the level of the water outside the cell indicates how much the pressure inside the cell exceeds the atmospheric pressure at the time of the experiment. This excess of pressure is due to the sugar particles in the cell, and is called the **osmotic pressure** of the solution.

What happens when the cell of sugar solution is immersed in pure water is that water from without enters the cell until the pressure of the water within and without is the same, viz., *one atmosphere.* The sugar particles, however, not being able to diffuse out through the semi-permeable wall of the cell, add their pressure to that of the water, and force the liquid up the tube.

139. Laws of Osmotic Pressure.—*If the strength of the solution*, i. e., the number of particles of dissolved substance in a given volume of the solution, *is increased, the osmotic pressure increases proportionally.* Since the *strength* of a solution means the same as *density* in the case of gases, we see that *the osmotic pressure of a solution corresponds to gaseous pressure;* for the latter, as we learned in § 127, *is proportional to the density.*

Moreover, *the osmotic pressure of a solution increases proportionally to the absolute temperature,* as in the case of gaseous pressure (*cf.* § 128).

Substances in dilute solution have, therefore, many of the properties which they would have if they were gases and had a volume equal to that of the solution.

140. Exercises.

1. What will be the volume at 0° C. of a mass of gas which at 20° C. has a volume of 102 c.c.?

2. How many c.c. of a gas measured at 28° C. are required to fill a 50 c.c. eudiometer at 0° C.?

3. One liter of air at 15° C. will have what volume at 25° C.?

4. A mass of air measures 70 c.c. when the barometric height is 740 mm. If the temperature remains constant, what volume ought the air to have when the barometer reading is 760 mm.? When it becomes 650 mm.?

5. What will be the volume at 800 mm. of a quantity of nitrogen which at 730 mm. measures 1.2 liters?

6. A quantity of hydrogen which measures 45 c.c. at 18° C. and 730 mm. will have what volume at 0° C. and 760 mm.?

7. 90 c.c. of air at 20° C. become, when heated, 150 c.c. To what temperature was the air heated?

8. A gas measures 20 liters at 10° C. and 760 mm. pressure. What volume will it have at 30° C. and 720 mm.?

9. The weight of a liter of nitrogen at standard conditions being about 1.25 grams, that of 1 liter of hydrogen, .09 grams, and that of 1 liter of chlorine, 3.18 grams, what, upon the basis of Avogadro's hypothesis, are the *relative* weights of the molecules of nitrogen, hydrogen, and chlorine?

10. If in Problem 9 we call the weight of the hydrogen molecule 2, what will be the *relative* weights of the molecules of nitrogen and chlorine?

CHAPTER XI.

AMMONIA.

141. Existence. — Ammonia is found in nature in very small quantities. As already stated (*cf.* § 112) electric discharges in moist air produce ammonia, nitrous acid, and nitric acid; consequently ammonia and its compounds, ammonium nitrite and ammonium nitrate, are found in the atmosphere and in rain water.

Small amounts of ammonium compounds are found in plants and in animal secretions.

142. Laboratory Method of Preparation. — In the laboratory, ammonia gas may be made either (1) by heating an ammonium salt with slaked lime, or (2) by warming concentrated ammonium hydroxide solution.

The first method is generally carried out as follows: —

About equal parts of an ammonium salt, *e. g.*, the *chloride* or the *sulphate*, and slaked lime are mixed together in a flask, just enough water being added to make a *thick* paste. The flask is connected, as shown in Fig. 32, with bottles containing water. None of the connecting tubes, except the last, dips below the surface of the water.

When the generating flask is heated, the evolved ammonia charges the water of the collecting bottles, forming ammonia water. The first bottle, especially, will show a rise of temperature and an increase of volume.

If the gas evolved from the flask is passed through bottles or U-tubes filled with *quicklime* or with ***solid sodium hydroxide***, it may be used for studying the properties of *dry* ammonia.

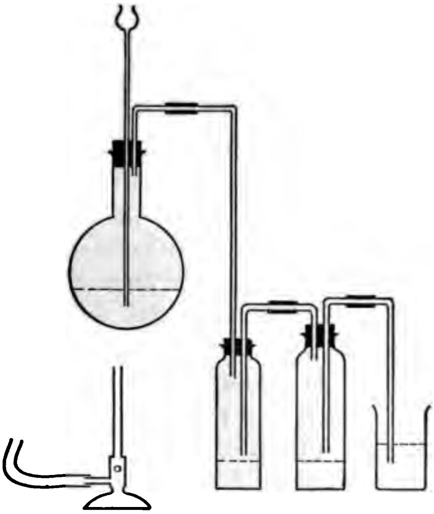


FIG. 32.

The **second method** for producing ammonia gas is more convenient. It consists simply in heating a small amount of concentrated ammonium hydroxide solution. Much ammonia gas is evolved, and may be dried in the usual way.

Calcium chloride may not be used to dry ammonia, for the reason that ammonia and calcium chloride form a crystalline compound of the formula $CaCl_2 . 8\ NH_3$.

The reaction between slaked lime and ammonium chloride is represented by the equation, —

$$2\ NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\ NH_4OH.$$

The ammonium hydroxide breaks up readily into *ammonia* and water, —

$$NH_4OH \longrightarrow NH_3 + H_2O.$$

143. Commercial Sources of Ammonia. — The two chief sources of ammonia are: —

(1) The *dry distillation of animal matter* (bones, skin-products, etc.).

(2) The *dry distillation of soft coal.*

Formerly all ammonia and all ammonium compounds were made by the *dry distillation* of animal matter; hence the name "spirits of hartshorn," "*spirit*" meaning a distillate, and "*hart*" being a general term for "deer," etc. The horns, bones, hoofs, hides, hair, etc., of animals contain nitrogenous bodies, which give much ammonia when heated with quicklime without access of air.

This method is used in many places, especially since the old method of making illuminating gas has been abandoned, to convert into a valuable product almost worthless scraps of animal matter.

The *most common source* of ammonia for many years has been the wash liquors of the gas works. Illuminating gas is made in the old process by the *dry distillation of soft coal.* At first it contains many impurities, among them ammonia, hydrogen sulphide, and carbon dioxide; these are removed by passing the gas through water. When the wash water, containing ammonium sulphide, ammonium carbonate, etc., is heated with slaked lime, ammonia gas is evolved.

Ammonia comes into the market as ammonia water (ammonium hydroxide), as ammonium salts, and also in the liquid state. To produce ammonium salts we treat ammonia water with acids until the solution is neutral, and then evaporate the water.

Thus, ammonium chloride (sal ammoniac) results when the neutralized solution of ammonium hydroxide and hydrochloric acid is evaporated; ammonium nitrate and sulphate are formed if nitric acid and sulphuric acid, respectively, are used.

The equations representing the formation of these salts are as follows: —

$$NH_4OH + HCl = NH_4Cl + H_2O.$$
$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O.$$
$$2\ NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2\ H_2O.$$

144. Physical Properties. — Ammonia is a colorless gas of characteristic odor. One liter of it under standard conditions weighs 0.762 grams; ammonia is therefore 0.59 as heavy as air.

Ammonia gas is *very* soluble in water, 1 c.c. of water absorbing, at standard conditions, 1,146 c.c. or 0.873 gram of the gas. The specific gravity of a 35% solution at 15° C. is about 0.88; that of the so-called 28° Beaumé solution is about 0.90.

Dry ammonia rushes into cold water as into a vacuum, and is likewise very soluble in alcohol and in ether. Charcoal can take up under favorable conditions about ninety times its own volume of ammonia gas.

145. Liquefaction of Ammonia. — The critical temperature of ammonia is far above the ordinary temperature, hence the gas may be liquefied by pressure. A simple apparatus for condensing ammonia is shown in Fig. 33.

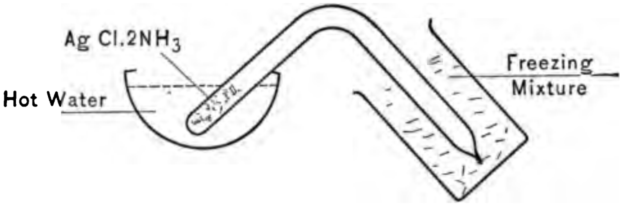
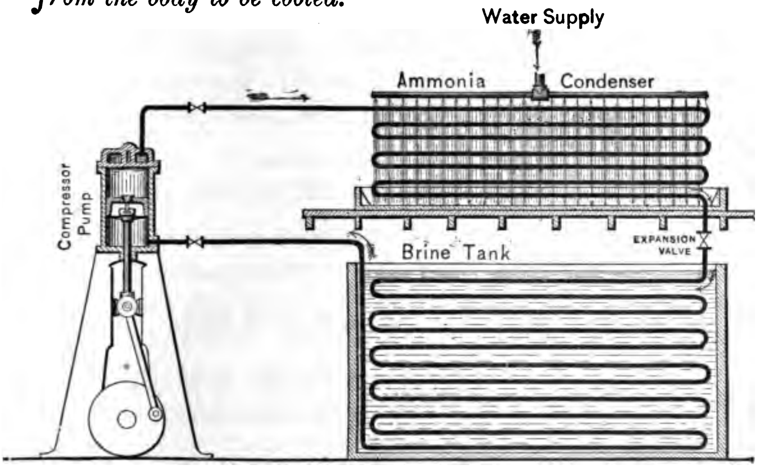


FIG. 33.

A small amount of the compound which silver chloride forms with ammonia, viz., AgCl. 2 NH_3, is placed in the rounded end of the bent tube. The tube is then sealed, and the end containing the silver ammonium compound is warmed in a water bath, while the drawn-out end is cooled in a freezing mixture. The compound containing the ammonia is thus decomposed, and the ammonia is condensed in the drawn-out end.

Liquid ammonia is about 0.6 as heavy as water. It boils at —40° C. under ordinary pressure, and freezes at —75° C.

146. Liquid Ammonia as a Refrigerating Agent. — The chief use of liquid ammonia is as a refrigerating agent, and to produce artificial ice. For this purpose gaseous ammonia (produced by heating ammonia water) is condensed to the liquid state, and the liquid ammonia is then allowed to evaporate rapidly. The heat necessary for the vaporization of the ammonia is *absorbed from the body to be cooled.*



MECHANICAL COMPRESSION SYSTEM.

FIG. 34.

The apparatus shown in Fig. 34 gives, in principle, the construction of a refrigerating system.

The compression engine forces gaseous ammonia into condensing pipes under so great a pressure that the ammonia is liquefied. The condensing pipes are cooled by streams of water. The liquid ammonia is then allowed to expand in another system of pipes surrounded by brine (concentrated salt solution); as a result the brine is cooled to a little above its freezing point, which is —21° C. When tanks containing water are placed in the cold salt solution, the water is frozen.

Instead of ammonia, liquid sulphur dioxide, liquid carbon dioxide, compressed air, etc., are often used to produce artificial ice.

147. Chemical Properties. — Ammonia does not burn in the air, but it burns readily in oxygen. The products are chiefly nitrogen and water, according to the equation,

$$2\ NH_3 + 3\ O \longrightarrow 3\ H_2O + N_2.$$

Chlorine reacts energetically with ammonia, forming nitrogen and hydrochloric acid. The equation is,

$$2\ NH_3 + 3\ Cl_2 \longrightarrow N_2 + 6\ HCl.$$

If the ammonia is present in excess, the hydrochloric acid unites with some of it, forming ammonium chloride. The complete equation is, therefore,

$$8\ NH_3 + 3\ Cl_2 \longrightarrow 6\ NH_4Cl + N_2.$$

A similar reaction occurs between ammonia and bromine.

Ammonia gas and hydrochloric acid gas unite in equal proportions by volume to form **solid** *ammonium chloride.*

148. Ammonium Compounds. — In the compounds which ammonia forms with hydrochloric acid, nitric acid, sulphuric acid, and water, the ammonia and the other substance are united *directly*. The resulting substances, ammonium chloride (NH_4Cl), ammonium nitrate (NH_4NO_3), ammonium sulphate [$(NH_4)_2SO_4$], and ammonium hydroxide (NH_4OH), might be called "ammonia hydrochlorate, hydronitrate," etc., but are not. Instead, they are looked upon as compounds of the *group* of elements, NH_4, with the element Cl and the radicals NO_3, SO_4, and OH. They are therefore called, as above, **ammonium** chloride, nitrate, etc.

The group NH_4 has not been isolated, since it breaks up immediately (*cf.* § 379) into ammonia and hydrogen; but its compounds are so like those of many metals that the group is called a *metallic radical.*

To what extent ammonium resembles the metals sodium and potassium will be seen by a comparison of some of its compounds with the corresponding compounds of these two metals. The formulas of some of these compounds are given below.

	AMMONIUM.	SODIUM.	POTASSIUM.
Chloride.	NH_4Cl	$NaCl$	KCl
Nitrate.	NH_4NO_3	$NaNO_3$	KNO_3
Sulphate.	$(NH_4)_2SO_4$	Na_2SO_4	K_2SO_4
Hydroxide.	NH_4OH	$NaOH$	KOH
Carbonate.	$(NH_4)_2CO_3$	Na_2CO_3	K_2CO_3
Phosphate.	$(NH_4)_3PO_4$	Na_3PO_4	K_3PO_4

149. Dissociation of Ammonium Compounds. — All ammonium compounds decompose readily, liberating ammonia, but the temperature of dissociation varies greatly in different cases.

Thus, the union of ammonia with water in ammonium hydroxide is so weak that ammonium hydroxide cannot be isolated, although it is probably present in an aqueous solution of ammonia.

The *ammonium salts* are more stable than the hydroxide, but even these decompose readily.

Ammonium chloride, for example, dissociates completely at 350° C. into ammonia and hydrochloric acid ; above 350° C., therefore, ammonium chloride cannot exist.

When the substance with which the ammonia is combined is not *volatile* at the temperature of dissociation, the heating of an ammonium compound simply causes ammonia to be liberated.

Thus, *ammonium phosphate* breaks up when heated into ammonia and phosphoric acid. Here the ammonia, being gaseous, escapes ; but the non-volatile phosphoric acid remains behind.

If, however, the substance with which the ammonia is united is volatile at the temperature of dissociation, the ammonium salt *sublimes*.

By **sublimation** we mean the distillation of a *solid*.

This is the case with ammonium chloride ; heat breaks it up into ammonia a[illegible]drochloric acid, but both these substances being vol[illegible], they pass off together and unite again when cold to form solid ammonium chloride.

This dissociation of ammonium compounds explains the liberation of ammonia from ammonium salts by "strong" bases. When ammonium chloride, for example, and slaked lime, $Ca(OH)_2$, are heated together, the ammonium chloride is *dissociated* into ammonia and hydrochloric acid, just as when it is heated by itself. The slaked lime, however, "*fixes*" the acid by forming with it calcium chloride and water (*cf.* § 142). As a result, only ammonia and some water pass off, calcium chloride remaining behind.

Similar reactions occur when sodium hydroxide, potassium hydroxide, etc., are used in place of slaked lime.

150. Composition of Ammonia. — Ammonia consists of nitrogen and hydrogen united in the proportion, **by weight,** of 14 parts nitrogen to 3 parts hydrogen. This fact is indicated by the formula NH_3.

The **volumetric** composition of ammonia may be proved in several ways: —

(1) By synthesis from nitrogen and hydrogen.
(2) By the action of chlorine on ammonia.

151. Synthesis of Ammonia from Nitrogen and Hydrogen. — If the two gases, nitrogen and hydrogen, mixed in the proportion of 1 volume of nitrogen to 3 of hydrogen, are subjected to the electric discharge, they combine in part to form ammonia; the union cannot, however, be made *complete*, no matter how long the "sparking" is continued. This is [illegible] to the fact that a point is soon reached at which as much of the ammonia is decomposed in a given time as is formed in the same time by the union of nitrogen and hydrogen. To make the combination complete it is necessary to remove the ammonia *as fast as it is formed.*

This may be done by "sparking" the mixture of nitrogen and hydrogen over some substance, *e. g.*, sulphuric acid, capable of absorbing the ammonia. Under these conditions all of the nitrogen and hydrogen disappears.

It is thus proved that 1 volume of nitrogen unites with 3 volumes of hydrogen to form ammonia. The union is accompanied by a *shrinkage in volume*, 4 volumes of the mixed gases becoming 2 volumes of ammonia.

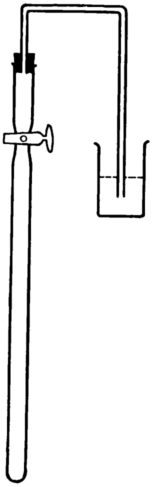


FIG. 35.

152. Action of Chlorine on Ammonia. — Since 1 volume of chlorine unites with 1 of hydrogen (*cf.* § 94), the relation of nitrogen to hydrogen can be obtained readily if that of nitrogen to chlorine can be established. For this purpose we make use of the known action of chlorine upon ammonia (*cf.* § 147). The experiment is carried out as follows: —

A Hoffmann tube (Fig. 35) is filled first with a saturated solution of sodium chloride in water, and then, by displacement of the salt solution, with chlorine.

The stopcock is then closed, and the cup above the stopcock is filled with concentrated ammonium hydroxide solution. The latter is now run, drop by drop, into the chlorine, care being taken that no air enters and no chlorine escapes. A flash of light will be seen when the first drops of ammonia water are introduced.

When almost all of the ammonia water has been run in, the stopcock is closed and the cup is filled with water. The cup is now connected, by means of a tube filled with water, with a beaker of dilute sulphuric acid, the stopcock is again opened, and the water and dilute acid are allowed to enter until the pressures inside and outside the tube are equalized.

The tube, which was full *of chlorine, will now be* one-third *full of nitrogen.* Hence.—

Volume of nitrogen : volume of chlorine :: 1 : 3 ; whence
Volume of nitrogen : volume of hydrogen :: 1 : 3.

153. Exercises.

1. How many grams of ammonia gas can be made by heating 100 grams ammonium chloride with slaked lime? How many liters at 0° C. and 760 mm.?

2. What weight of ammonium sulphate is required to give, with lime, 20 liters of ammonia gas when one liter of ammonia weighs 0.77 grams?

3. What weight of slaked lime, $Ca(OH)_2$, is necessary to decompose 50 grams ammonium nitrate? How many grams ammonia will be formed?

4. May concentrated sulphuric acid be used to dry ammonia gas? Why?

5. How could you separate a mixture of the gases ammonia, oxygen, and nitrogen so as to get the proportionate amounts of each in the mixture?

6. What would be the volume of each of the resulting gases

if 500 c.c. of ammonia gas were completely decomposed into its constituents ?

7. How many cubic centimeters of oxygen will be required to unite exactly with the hydrogen produced by the complete decomposition of 100 c.c. of ammonia gas ?

CHAPTER XII.

NITROGEN ACIDS AND OXIDES.

154. Nitric Acid. — Nitric acid is one of the most important substances known to Chemistry. It has been in use since the time of the early alchemists, but its true nature was not understood until the latter part of the eighteenth century.

During the Middle Ages nitric acid was made by the distillation of a mixture of alum, blue vitriol, and niter.

Alum is potassium aluminum sulphate *plus* crystal-water [K_2SO_4, $Al_2(SO_4)_3$, 24 H_2O], and blue vitriol is cupric sulphate *plus* crystal-water ($CuSO_4$. 5 H_2O); by the dry distillation of these substances sulphuric acid was set free. This with the niter (KNO_3) gave nitric acid.

155. Commercial Preparation. — At the present time nitric acid is made on a large scale by heating sodium nitrate with concentrated sulphuric acid. The operation is carried out in large iron retorts; and the vapors evolved are condensed in a system of earthenware jars. The resulting liquid is redistilled.

In this way there is obtained an acid of specific gravity 1.4; its boiling point is 120° to 121° C. This, the "commercial" grade of nitric acid, is only 68%, by weight, nitric acid. The remainder is water.

156. Laboratory Method. — In the laboratory, nitric acid is commonly made by heating potassium nitrate with concentrated sulphuric acid in a retort or distilling bulb connected with a condenser. The condenser may be a test tube partly immersed in water, as in Fig. 36. When no more acid distills over, the flask is allowed to cool; the other product of the reaction, potassium hydrogen sulphate ($KHSO_4$), then crystallizes out in the form of long, white needles.

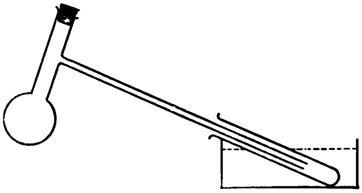


FIG. 36.

The equation for the reaction is, —

$$\underset{101}{KNO_3} + \underset{98}{H_2SO_4} \longrightarrow \underset{136}{KHSO_4} + \underset{63}{HNO_3}.$$

For the reaction between sodium nitrate and sulphuric acid the equation is, —

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3.$$

157. Preparation of Nitric Acid Compared with that of Hydrochloric Acid. — The preparation of nitric acid resembles that of hydrochloric acid. In each case the acid is set free from its salts by sulphuric acid, *not* because sulphuric acid is *stronger* than the acid it displaces, but because hydrochloric acid and nitric acid are *volatile*, and are, therefore, removed from the "field of action." As a result, the reaction goes on until practically complete (*cf.* § 151).

In *each* of these cases only *half* of the hydrogen of sulphuric acid is replaced by the metallic element. If the temperature is raised considerably, a second portion of sodium nitrate will react with the sodium hydrogen sulphate formed, giving *normal* sodium sulphate and a second portion of nitric acid, according to the equation,

$$NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3.$$

In the treatment of sodium *chloride* with sulphuric acid on a commercial scale, this second reaction is actually carried out, because the compound Na_2SO_4 is wanted. In the preparation of nitric acid, however, the second reaction is of no advantage, since the high temperature necessary decomposes the nitric acid.

158. Properties of Nitric Acid. — Commercial nitric acid is dehydrated by distilling it with concentrated sulphuric acid. The anhydrous acid (the best yet made was probably 99.8% pure) is a thick, colorless oil of specific gravity 1.56. It begins to distill at 86° C., but breaks up to a certain extent into other compounds. The equation for its decomposition is, —

$$2\ HNO_3 \longrightarrow 2\ NO_2\ (\text{or}\ N_2O_4) + H_2O + O.$$

Nitrogen dioxide is a brown gas which dissolves readily in nitric acid ; hence anhydrous nitric acid that has been distilled has a brown color. This color may be removed by bubbling air through the liquid.

The same decomposition of nitric acid takes place in the light (very rapidly in sunlight) ; hence the nitric acid of reagent bottles soon becomes brown.

When the vapors of nitric acid are passed through a hot tube they are completely decomposed into nitrogen dioxide, water, and oxygen.

As an acid, nitric acid neutralizes solutions of bases, forming with them *nitrates* and water, just as hydrochloric acid forms chlorides and water.

Thus, if potassium hydroxide solution is treated with dilute nitric acid until neutral, and the solution is evaporated, potassium nitrate will be obtained. The equation is, —

$$KOH + HNO_3 = KNO_3 + H_2O.$$

159. Action of Nitric Acid upon Metals. — The tendency of nitric acid to break up into oxides of nitrogen and free oxygen (*cf.* § 158) determines its general chemical behavior; for nitric acid is not only a strong acid, but a powerful **oxidizing agent.** When, therefore, we compare the action of nitric acid upon metals with that of hydrochloric and dilute sulphuric acids, we observe a great difference; for while the acids just named generally give up hydrogen when treated with metals, nitric acid rarely does so. Instead of being set free, the *nascent* hydrogen usually reduces some of the nitric acid to nitrogen oxides or, even lower, to ***hydroxylamine***, NH_2OH, and to ammonia.

Thus, zinc and dilute nitric acid (5% to 6%) give, perhaps, zinc nitrate and hydrogen, according to the equation,

$$Zn + 2\,HNO_3 \longrightarrow Zn(NO_3)_2 + H_2 \text{ (cf. § 9)};$$

but no hydrogen is liberated. Instead, the hydrogen formed reduces some of the nitric acid to ammonia. Hence the solution contains, besides water, zinc nitrate and ammonium nitrate. The following equations probably represent what takes place:

(1) $4\ Zn + 8\ HNO_3 = 4\ Zn(NO_3)_2 + 4\ H_2$;
(This is the equation above multiplied by 4.)
(2) $4\ H_2 + HNO_3 = NH_4OH + 2\ H_2O$;
(3) $NH_4OH + HNO_3 = NH_4NO_3 + H_2O$.
Hence the complete equation must be,
$4\ Zn + 10\ HNO_3 = 4\ Zn(NO_3)_2 + NH_4NO_3 + 3\ H_2O$.

In solutions somewhat more concentrated than the above the reduction of nitric acid goes only to nitrogen oxides. The equation for the most common reduction of nitric acid by nascent hydrogen is, probably, —

$$2\ HNO_3 + 3\ H_2 \longrightarrow 4\ H_2O + 2\ NO.$$

Copper and nitric acid of specific gravity 1.2 do not react according to the equation,

$$Cu + 2\ HNO_3 = Cu(NO_3)_2 + H_2,$$

for the reaction is an oxidation: —

$$3\ Cu + 2\ HNO_3 \longrightarrow 3\ CuO + 2\ NO + H_2O.$$

Copper nitrate is indeed formed, 63 grams of copper giving 124 grams of copper nitrate, but *no hydrogen is evolved.* Instead of hydrogen we get a gas which, though colorless itself, forms brown fumes when it comes in contact with oxygen. This gas is *nitric oxide*, NO, and the brown fumes consist of nitrogen dioxide, NO_2; hence the copper must have reduced some of the nitric acid.

The cupric oxide then reacts with the nitric acid, giving cupric nitrate and water.

$$3\ CuO + 6\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 3\ H_2O.$$

way and gets into the soil. All the nitric acid of commerce, however, is made from the *nitrates;* these are found as natural deposits in certain places.

The "nitrate beds" were probably formed by the *oxidation*, through the agency of bacilli, of *nitrogenous organic matter in the presence of alkali.* The most extensive deposits of nitrates in the world are those of the Atacama Desert in Chile. The alkali present is sodium carbonate, hence Chile saltpeter is *sodium* nitrate and not the potassium salt.

164. Manufacture of Potassium Nitrate. — Potassium nitrate was formerly obtained almost exclusively from Asiatic countries, where it appeared as a deposit on the ground; but nowadays most of it is made from sodium nitrate. The process may be carried out as follows: —

Hot, fairly concentrated solutions of potassium chloride and sodium nitrate are mixed, and the resulting solution is poured off from the crystalline deposit of sodium chloride which separates out. The solution contains much potassium nitrate and small amounts of sodium chloride, etc. This impure potassium nitrate is then redissolved in as small an amount of hot water as possible, and allowed to crystallize out; by several recrystallizations pure potassium nitrate is obtained.

The equation representing the formation of potassium nitrate is, —

$$KCl + NaNO_3 \longrightarrow KNO_3 + NaCl.$$

It applies only to a mixture of concentrated solutions of the factors.

In certain European countries the farmers cultivate niter by introducing the proper micro-organisms into a mixture of alkali and nitrogenous matter.

165. Uses of Nitric Acid and the Nitrates. — Nitric acid has many important applications: nitrobenzene, glyceryl nitrate (nitroglycerine), and nitrates of cellulose (collodion, gun cotton, celluloid, etc.) are made by its agency.

The *nitrates* are used in the manufacture of gunpowder and various explosives, and in the preservation of meats.

Glyceryl nitrate (wrongly called nitroglycerine) is made by the action of a mixture of concentrated nitric and sulphuric acids at a low temperature upon glycerine. It is a thick, greenish oil of a very unstable nature, and very explosive. It is usually mixed with a porous earth, and appears in the market chiefly as *dynamite*.

Gun cotton and *collodion* are made by the action of a mixture of nitric and sulphuric acids upon cotton.

Celluloid is a mixture of gun cotton and camphor.

Nitrobenzene is made from benzene, C_6H_6, and the nitric-sulphuric acid mixture. When nitrobenzene is reduced by nascent hydrogen, it gives *aniline*, the starting material in the manufacture of the aniline dyes.

Potassium nitrate is important chiefly as a constituent of gunpowder, which, as was stated in § 26, is a physical mixture of potassium nitrate with sulphur and charcoal in various proportions. The exact amount of each of the constituents depends upon the purpose for

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trogen *trioxide*, but a mixture of the *dioxide* (NO_2) with *nitric oxide.*

***169. Nitrogen Dioxide and Nitrogen Tetroxide (NO_2 and N_2O_4).**—*Nitrogen dioxide* lies between nitrogen trioxide and nitrogen pentoxide as regards the proportion of oxygen it contains. Below 22° C. it is a liquid; but it is usually known in the form of its vapor.

Nitrogen tetroxide ("tetra" = four) exists at low temperatures, but it *dissociates* readily, to some extent even at 0° C., into nitrogen dioxide. This is shown in the equation,

$$N_2O_4 = 2\ NO_2.$$

The *degree* of the dissociation is shown by the darkening of the color, nitrogen tetroxide being colorless, but nitrogen dioxide brown.

When nitrogen tetroxide is dissolved in much cold water, the solution contains a mixture of nitrous and nitric acids; hence nitrogen tetroxide is the anhydride of both of these acids. The equation showing this fact is, —

$$N_2O_4\ (= 2\ NO_2) + H_2O \longrightarrow HNO_2 + HNO_3.$$

Nitrogen tetroxide is formed when lead nitrate, $Pb(NO_3)_2$, is heated. The vapors may be condensed by passing them through a U-tube surrounded by a freezing mixture. The decomposition of lead nitrate corresponds exactly with that of nitric acid, as is shown by the equation,

$$Pb(NO_3)_2 = PbO + N_2O_4 + O\ (cf.\ \S\ 158).$$

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*The names used are in accordance with the latest nomenclature.

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170. Nitric Oxide (NO). — Two other oxides of nitrogen are known, viz., *nitric oxide* and *nitrous oxide*; both are colorless gases at the ordinary temperature and pressure.

Nitric oxide is produced when nitric acid of specific gravity 1.2 is allowed to react with copper. The equation has already been given (*cf.* § 159). It is, —

$$3\ Cu + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO.$$

Nitric oxide is slightly heavier than air. One liter of it weighs, under standard conditions, 1.34 grams. The gas is only slightly soluble in water.

When nitric oxide is passed into a solution of ferrous sulphate, $FeSO_4$, large quantities of the gas are absorbed, a brown compound of ferrous sulphate and nitric oxide being formed. When the solution containing this compound is heated, pure nitric oxide escapes.

Nitric oxide becomes brown when it comes into contact with air or oxygen, owing to the formation of *nitrogen dioxide.*

One volume of nitric oxide consists of one-half a volume of nitrogen and one-half a volume of oxygen.

The amount of the nitrogen may be shown by heating a piece of metallic sodium in a measured volume of the gas over mercury (see Fig. 37). The sodium combines with the oxygen of the nitric oxide, leaving the nitrogen. *The volume of the nitrogen should be just half that of the nitric oxide taken.*

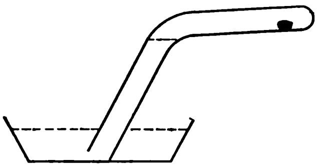


FIG. 37.

Nitric oxide supports the combustion of phosphorus and of magnesium, as well as of sodium.

171. Nitrous Oxide (N_2O). — Nitrous oxide is commonly made by heating ammonium nitrate (NH_4NO_3) to 170° C., or, better, by heating a mixture of sodium nitrate and ammonium sulphate to a slightly higher temperature.

The formation of nitrous oxide is the result of several reactions. At first the ammonium nitrate probably dissociates into ammonia and nitric acid just as ammonium chloride gives ammonia and hydrochloric acid. The ammonia and nitric acid do not, however, recombine when cool, because the nitric acid *oxidizes* the hydrogen of the ammonia to water.

The *final* equation for the decomposition of ammonium nitrate is, —

$$NH_4NO_3 \longrightarrow N_2O + 2\ H_2O.$$

Compare with this the equation for the decomposition of ammonium nitrite (§ 111). Note that *all* of the hydrogen is oxidized to *water* in each case, and that it is the oxygen in excess of that required to oxidize hydrogen that causes the formation of nitrous oxide when ammonium nitrate is decomposed.

Nitrous oxide is the only gas besides oxygen that will re-ignite a glowing splinter.

The *volumetric composition* of nitrous oxide may be determined in the same way as that of nitric oxide, viz., *by taking out the oxygen by means of sodium.* There is, however, a great difference in results; for while one volume of nitric oxide contains one-half a volume of nitrogen and one-half a volume of oxygen, one volume of nitrous oxide contains one volume of nitrogen and one-half a volume of oxygen.

Nitrous oxide may be condensed to the liquid form; as such it is a commercial article. When the pressure under which the gas is kept is removed, some of the liquid vaporizes, producing the "laughing gas" which dentists use to produce insensibility to pain.

Nitrous oxide is easily soluble; 1 volume of water at 0° C. absorbs 1.3 volumes of the gas. One liter at standard conditions weighs 1.97 grams.

172. Hyponitrous Acid, $(NOH)_2$. — Hyponitrites, *i. e.*, salts of hyponitrous acid, have been known for some time, but the acid itself has only recently been isolated. A solution of hyponitrous acid decomposes readily, giving nitrous oxide, according to the equation,

$$(NOH)_2 \longrightarrow N_2O + H_2O.$$

Nitrous oxide may thus be looked upon as *in some sense* the *anhydride* of hyponitrous acid; but the union of nitrous oxide and water to form the acid does not take place.

173. Exercises.

1. How many grams of nitric acid can be made, theoretically, from 1 kg. sodium nitrate with sulphuric acid?

2. What will be the volume of 28.4 grams of commercial nitric acid?

3. How much sulphuric acid (calculated as 100% H_2SO_4) will be needed to give 1,260 grams of nitric acid with potassium nitrate, if potassium hydrogen sulphate is formed?

4. Calculate the percentage composition of nitric acid?

5. How much potassium hydroxide is required to neutralize exactly a solution containing 42 grams nitric acid?

6. How could you separate a mixture of silver and gold chemically?

7. How many grams nitrogen tetroxide could be made from 450 grams lead nitrate? How much oxygen?

8. How many grams nitric oxide can be made, theoretically, from 100 grams nitric acid with copper? How much copper is needed? How much cupric nitrate is formed?

9. How many liters of nitrous oxide at 0° C. and 760 mm. can be made from 240 grams ammonium nitrate? How many at 20° C. and 720 mm.?

10. How would you distinguish between nitrous oxide and oxygen?

11. How many cubic centimeters of each of its constituents combine to form 100 c.c. nitric oxide? To form 100 c.c. of nitrous oxide?

12. Name three different classes of nitrates, basing the difference upon the way in which the members of each class decompose when heated.

CHAPTER XIII.

SULPHUR AND ITS COMPOUNDS.

174. Occurrence and Preparation of Sulphur. — Sulphur occurs in nature in both a free and a combined form. In the free condition it is obtained chiefly from Sicily, Mexico, and, to some extent, from Louisiana. Natural sulphur is usually found mixed with much earthy material, from which it must be separated to prepare it for the market.

The *first* operation in the purification of sulphur usually consists in heating the natural product; the sulphur melts and flows away, leaving the infusible impurities behind.

In the *second* operation the partially purified sulphur is distilled from large iron retorts (see Fig. 38), and is thus separated from less volatile impurities.

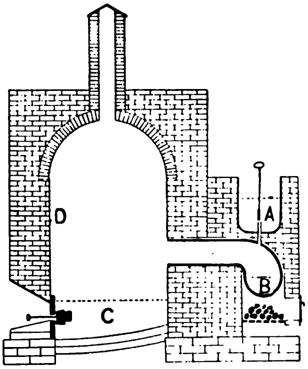


FIG. 38.

The melted sulphur in the reservoir *A* is allowed to flow from time to time into the retort *B*, in which the sulphur is vaporized. The sulphur vapor which passes into the condenser collects either in the liquid state, at the bottom (*C*) of the condenser, or in a solid state upon the cold walls (*D*). The *liquid* sulphur is run into molds to crystallize, thus producing the "roll-sulphur," or "brimstone" of commerce; the sulphur which solidifies upon the walls appears in the form of fine *meal* and is called "*flowers*" (more correctly, "*flour*") of sulphur.

175. Physical Properties. — Sulphur, like many other elements, exists in several different physical forms; consequently, in giving the properties of sulphur we must specify the *kind* of sulphur to which we are referring. The several varieties of sulphur may be grouped into three classes: —

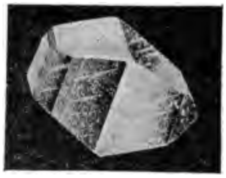


FIG. 39.

(1) **Ordinary,** or *rhombic*, sulphur (Fig. 39). This is the form that occurs in nature. All other forms *revert* to this form. Its specific gravity is 2.07.

(2) **Prismatic** sulphur (Fig. 40). This is formed by the *slow* cooling of fused sulphur of any of the other varieties. Its specific gravity is 1.96.

(3) **Amorphous** sulphur. This form is produced when sulphur at temperatures above 230° C. is chilled *rapidly*, as by pouring it into cold water.

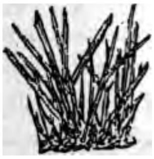


FIG. 40.

At ordinary temperatures amorphous sulphur changes *slowly* (after some days) into the ordinary form; at about

100° C., however, the change is *instantaneous*, and much heat is evolved. Ordinary and prismatic sulphur are readily soluble in carbon disulphide, CS_2; but amorphous sulphur is partly insoluble in that liquid.

The form known as "flowers" of sulphur is both crystalline and amorphous. It consists of a crystalline kernel and an amorphous covering.

The existence of an element in several forms is called **allotropism,** and the different varieties of the element are called its *allotropic* forms (*cf.* § 263).

Ordinary sulphur has a yellow color and is practically without odor and taste. It is soluble to a slight extent in ether and in alcohol, but is insoluble in water. The best solvent for sulphur is carbon disulphide; 100 parts of this substance dissolve 46 parts of sulphur at the ordinary temperature.

Ordinary sulphur behaves *peculiarly* when heated. At 114° C. it melts, becoming a yellow liquid. As the heating is continued the sulphur becomes more viscous and dark-colored; at 250° C. it is almost black and can hardly be poured. Above 300° C. it is limpid again, and at 448° it boils, forming a yellow vapor.

176. Chemical Properties. — Sulphur unites directly with many elements, especially with metals. Thus, when a mixture of powdered iron and sulphur is heated, or moistened with water, or strongly compressed, it unites chemically, forming ferrous sulphide, FeS. Similarly, copper foil burns in sulphur vapor, giving copper sulphide. Mercury combines with sulphur when the two are simply *triturated*, i. e., rubbed together in a mortar.

There are many *common* illustrations of the action of sulphur upon metals. Thus, silver egg-spoons are blackened by the sulphur contained in eggs; and silver coins which have been carried about in the pockets are colored by the sulphur of the perspiration.

The illuminating gas of many cities contains sulphur compounds; this fact accounts for the tarnishing of articles of brass, copper, lead, silver, etc., in houses in which such gas is used.

At about 260° C. sulphur begins to unite with the oxygen of the air. If sulphur at a temperature slightly below 260° C. is examined in the dark it will be found to **phosphoresce,** i. e., *glow*.

In burning, sulphur produces sulphur *dioxide*, SO_2. This is an invisible gas having the characteristic odor of burning sulphur.

177. Uses of Sulphur. — Sulphur is used in the preparation of many important substances. Thus, *rubber goods* and *vulcanite* are made by heating together caoutchouc and sulphur; *match tips*, especially the older forms, contain sulphur as an ingredient; *gunpowder*, as previously stated, is a mixture of charcoal, sulphur, and niter; and sulphur dioxide, which is used for *bleaching* and as a *germicide*, is made by burning sulphur in air.

Finally, sulphur is used in the preparation of *sulphuric acid*, which is possibly the most important substance manufactured.

178. Compounds of Sulphur. — Sulphur is a constituent of many important compounds; for the *sulphides*, next to the oxides, are the most common ores of the metals. Among the natural sulphides are *iron pyrites* (FeS_2), *galena* (PbS), and *hydrogen sulphide* (H_2S). The latter is a gas under ordinary conditions.

The two important *oxides* of sulphur are *sulphur dioxide* and *sulphur trioxide.*

With hydrogen and oxygen sulphur forms *sulphuric acid* and other acids, and with metals and oxygen, *sulphates*, *sulphites*, *thiosulphates*, etc.

The most important *natural* sulphate is *gypsum*, $CaSO_4 . 2\ H_2O$. Natural barium sulphate, $BaSO_4$, is called "*heavy spar.*" Both are important minerals.

Iron pyrites, FeS_2, is a source of both sulphur and sulphur dioxide. When it is *roasted*, i. e., heated in a current of air, its sulphur is oxidized to sulphur dioxide, SO_2, but if the iron pyrites is heated *without access of air* it breaks down into a compound of iron and sulphur containing only two-thirds of the sulphur of the original pyrites. The excess of sulphur is liberated.

The equation representing this reaction is, —

$$3\ FeS_2 = Fe_3S_4 + 2\ S.$$

The reaction is like that which takes place when manganese dioxide is heated (*cf.* § 21), and which is indicated by the equation,

$$3\ MnO_2 = Mn_3O_4 + O_2.$$

179. Hydrogen Sulphide. — Hydrogen sulphide, or *hydrosulphuric acid*, is a colorless gas composed of hydrogen and sulphur in the proportion of 1 part by weight of hydrogen to 16 parts of sulphur. This fact is shown by the formula, H_2S.

Hydrogen sulphide is usually prepared by the action of dilute sulphuric or hydrochloric acid upon iron sulphide. The reactions are shown by the equations,

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S, \text{ and}$$
$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S.$$

The iron sulphate or chloride formed remains in solution.

The method just described gives hydrogen sulphide in a form good enough for ordinary use, *but not pure.* Pure hydrogen sulphide is prepared by the action of concentrated hydrochloric acid upon antimony trisulphide, Sb_2S_3. The equation is, —

$$Sb_2S_3 + 6\,HCl \longrightarrow 2\,SbCl_3 + 3\,H_2S.$$

180. Properties of Hydrogen Sulphide. — Hydrogen sulphide has the odor of rotten eggs. It is formed by the decomposition of most organic substances containing sulphur. So-called "sulphur" waters owe their properties to the hydrogen sulphide dissolved in them.

The gas is 1.18 times as heavy as air.

Hydrogen sulphide is very soluble in water; one volume of water absorbs at standard conditions three volumes of the gas. The aqueous solution is readily decomposed, especially in the light and when warm, by the oxygen of the air. The hydrogen is thus converted into water, and the sulphur is set free; consequently a solution of hydrogen sulphide soon loses its odor and deposits sulphur. The equation is, —

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S.$$

Similar to the action of oxygen is that of chlorine, which forms with hydrogen sulphide or its aqueous solution hydrochloric acid and sulphur, according to the equation,

$$H_2S + Cl_2 \longrightarrow 2\,HCl + S.$$

Iodine acts in the same way, viz.: —

$$H_2S + 2\,I \longrightarrow 2\,HI + S.$$

This method is used for the preparation of hydriodic acid. Hydrogen sulphide is, as we might expect, a *reducing agent.*

181. Sulphides.—Hydrogen sulphide is a weak *acid*, and is therefore called *hydrosulphuric acid.* Its salts, the *sulphides*, may be formed in several ways; these are, —

(1) By the *reduction* of a sulphate or sulphite;

(2) By the *neutralization* of an alkali with hydrogen sulphide;

(3) By the *addition of hydrogen sulphide* to a soluble salt of the metal whose sulphide is to be formed.

An illustration of the *first method* is the reduction of sodium sulphate, when heated with charcoal, to *sodium sulphide.* The equation is, —

$$Na_2SO_4 + 4\,C \longrightarrow Na_2S + 4\,CO.$$

An illustration of the *second method* is the absorption of hydrogen sulphide by a solution of sodium hydroxide. The equation is, —

$$2\,NaOH + H_2S \longrightarrow Na_2S + 2\,H_2O.$$

Hydrosulphides. — The equation just given represents only the *final* products formed in the ordinary method of preparing sodium sulphide; for, if we pass hydrogen sulphide into sodium hydroxide solution until no more hydrogen sulphide is absorbed, we obtain *sodium hydrosulphide*, NaSH. The equation is, —

$$NaOH + H_2S = NaSH + H_2O.$$

If we now add to the sodium hydrosulphide as much sodium hydroxide as we used originally, we shall obtain *sodium sulphide*, Na_2S, as is represented in the equation,

$$NaOH + NaSH = Na_2S + H_2O.$$

To prepare *ammonium sulphide*, $(NH_4)_2S$, we employ a similar method.

182. Precipitation of Sulphides. — The *third method* of forming a sulphide, viz., by adding hydrogen sulphide to a soluble salt of the metal, will succeed *only in case the sulphide desired is insoluble in the solvent present.* Thus if hydrogen sulphide, either in gaseous form or in aqueous solution, is added to a solution of cupric sulphate, $CuSO_4$, cupric sulphide and sulphuric acid are formed, according to the equation,

$$CuSO_4 + H_2S \longrightarrow \mathit{CuS} + H_2SO_4.$$

The cupric sulphide will appear as a black precipitate. In future we shall usually *italicize* the formula of a precipitate.

Explanation. — The student will notice that *in every case* the action of hydrogen sulphide upon the salt of a metal must *tend* to produce a *free acid* in addition to the sulphide of the metal. Now, we know that free acids generally act upon sulphides giving hydrogen sulphide, this being in fact the way in which hydrogen sulphide is prepared (*cf.* § 179); hence the precipitation of cupric sulphide from a solution of cupric sulphate by hydrogen sulphide must be possible only because the *cupric sulphide is insoluble in the dilute acid* formed at the same time.

Sulphides that are soluble in dilute acids cannot, therefore, be precipitated, or only *incompletely*, by hydrogen sulphide.

Thus, no precipitate is produced when hydrogen sulphide is added to manganese sulphate solution, because the *reverse* reaction, represented by the equation,

$$MnS + H_2SO_4 \longrightarrow MnSO_4 + H_2S,$$

is the one that tends to take place. If, however, we use, instead of hydrogen sulphide, a soluble salt of hydrogen sulphide, precipitation of manganese sulphide occurs, for the reaction *cannot* produce free acid.

Thus, with sodium sulphide the reaction is represented by the equation,

$$MnSO_4 + Na_2S \longrightarrow \mathit{MnS} + Na_2SO_4.$$

Some sulphides, however, are soluble in water itself; such sulphides cannot, of course, be precipitated by either hydrogen sulphide or its salts. *Barium and calcium sulphides* are examples.

183. Carbon Disulphide (CS_2). — Carbon disulphide is formed by the direct union of carbon and sulphur, the usual method being to pass sulphur vapor over hot charcoal.

When pure, carbon disulphide is colorless and has an ethereal odor; but as obtained commercially it is often yellow and has a disagreeable smell. The liquid boils at 47° C.

Carbon disulphide is very inflammable. The products of its combustion are *carbon dioxide* and *sulphur dioxide*, as represented by the equation,

$$CS_2 + 3\ O_2 = CO_2 + 2\ SO_2.$$

The chief use of carbon disulphide is as a solvent for sulphur, caoutchouc, phosphorus, iodine, etc.

184. Manufacture of Sulphuric Acid. — The modern method of making sulphuric acid is to treat sulphur trioxide with water (*cf.* § 190). The so-called "English," or common, process consists in *oxidizing sulphur dioxide in the presence of water.*

The oxidizing agent used is nitric acid. The sulphur dioxide is produced from sulphur, iron pyrites (FeS_2), or galena (PbS): its oxidation is carried out in large boxes lined with lead and called "the leaden chambers." Currents of air, of steam, and, occasionally, of nitric acid enter the leaden chambers along with the sulphur dioxide, and sulphuric acid is the result The simplest equation is, —

$$SO_2 + H_2O + O \longrightarrow H_2SO_4.$$

Explanation. — The nitric acid introduced into the leaden chambers is reduced to *nitric oxide*, NO; a small amount of sulphur dioxide is thus oxidized directly by nitric acid. But the greater portion of the oxygen used comes from the air; for the nitric oxide takes up the oxygen of the air, forming nitrogen dioxide (*cf.* § 170), and then gives up the oxygen to the sulphur dioxide. All of these facts are represented by the following equations: —

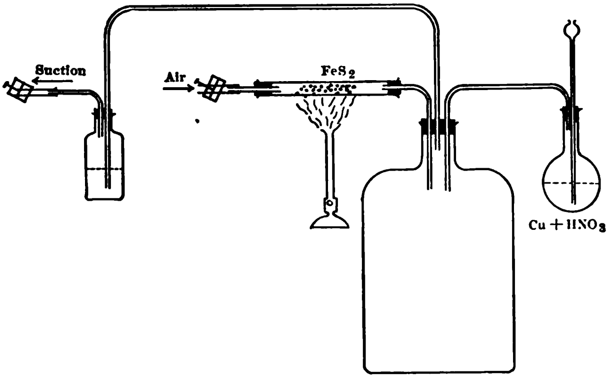


FIG. 41.

(1) $SO_2 + 2\,HNO_3 = H_2SO_4 + 2\,NO_2$.
(2) $NO_2 + SO_2 + H_2O = H_2SO_4 + NO$.
(3) $2\,NO + O_2 = 2\,NO_2$.
(4) Repetition of (2).

Theoretically, a very small amount of nitric acid ought to be able to oxidize an indefinitely large amount of sulphur dioxide, but in practice some of the nitrogen oxides are lost; hence nitric acid must be added from time to time to the mixture in the leaden chambers. The greater portion of the nitrogen oxides is prevented from escaping by being made to pass through towers of dilute sulphuric acid, which absorbs them. They are thus compelled to perform the work of oxidizing sulphur dioxide over and over again.

The equations given above are only incomplete representations of the reactions taking place in the leaden chambers.

It is *probable* that the nitric oxide reacts with the steam, oxygen and sulphur dioxide present in the leaden chambers, giving a substance called *nitrosyl sulphuric acid.* The equation is, —

$$2\,SO_2 + 2\,NO + 3\,O + H_2O = 2\,NO.HSO_4.$$

The nitrosyl sulphuric acid is a solid substance. It is known technically as "chamber crystals." It is readily decomposed by the excess of steam, giving sulphuric acid and nitrogen trioxide (N_2O_3), as is shown by the equation,

$$2\,NO.HSO_4 + H_2O = 2\,H_2SO_4 + N_2O_3.$$

Apparatus for demonstrating the nitrosyl sulphuric acid manufacture is shown in Fig. 41.

185. Purification of Sulphuric Acid. — The sulphuric acid obtained in the leaden chambers contains about 40% of water; it is therefore concentrated by evaporation. The evaporation is carried out in *leaden pans* until the acid is concentrated enough to attack the lead. When this is the case, further evaporation is carried out in *cast-iron* pans until an acid containing about 13% of water is obtained. This is the "crude" sulphuric acid of commerce. It is very impure. If the acid is to be concentrated still further, the evaporation must be carried out in vessels of *glass*, *porcelain*, or *platinum.*

The pure acid is made by distilling the crude product in stills of platinum lined with gold. There is thus obtained an oil boiling at 338° C. and containing only 1.5% water. Its specific gravity is 1.854 at 0° C. The anhydrous acid (approximately 100% sulphuric acid) is made only in very small amounts.

186. Properties. — Sulphuric acid is a thick, oily, colorless liquid. When it is diluted with water, much heat is evolved, so much, indeed, that the water sometimes boils. To avoid spattering of the hot liquid we pour the concentrated acid in a small stream *into the water*, not the water into the acid.

Sulphuric acid forms several **hydrates** with water, the two most important being those represented by the formulas, $H_2SO_4 . H_2O$ and $H_2SO_4 . 2 H_2O$. Because of the tendency of sulphuric acid to take up water, it is used as a *drying agent.*

The dehydrating power of sulphuric acid also accounts for the fact that organic matter, *e. g.*, paper, wood, dust, sugar, etc., are *charred* by it. These bodies are compounds containing carbon, hydrogen, and oxygen (*cf.* § 52). The hydrogen and oxygen are abstracted, *as water*, by the acid, and charcoal is left.

187. Reduction of Sulphuric Acid. — Sulphuric acid decomposes, when sufficiently heated, much as nitric acid does; the products are chiefly sulphur dioxide, oxygen, and water. The equation

$$H_2SO_4 = H_2O + SO_2 + O$$

thus represents what takes place. If we have at hand a substance that can absorb oxygen, the decomposition of the acid takes place very easily. The reducing agents may be sulphur, charcoal, copper, mercury, etc.

The acid has no action upon these substances in the cold; but when it is heated with them the acid is reduced to sulphurous acid, *i. e.*, to sulphur dioxide and water. The reducing agents are, of course, oxidized.

The following equation represents what takes place when sulphur is heated with sulphuric acid: —

$$2\ H_2SO_4 + S = 2\ H_2SO_3 + SO_2 = 3\ SO_2 + 2\ H_2O.$$

With copper the equation is, —

$$H_2SO_4 + Cu = CuO + H_2O + SO_2.$$

The cupric oxide then reacts further with the sulphuric acid, giving cupric sulphate and water, —

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Hence the *complete* equation is, —

$$2\ H_2SO_4 + Cu = CuSO_4 + 2\ H_2O + SO_2.$$

Perhaps the equations for the action of copper upon hot, concentrated sulphuric acid are, —

(1) $Cu + H_2SO_4 = CuSO_4 + H_2$, and
(2) $H_2 + H_2SO_4 = 2\ H_2O + SO_2$.

In any case, the *complete* equation is as above,

$$Cu + 2\ H_2SO_4 = CuSO_4 + 2\ H_2O + SO_2.$$

Compare this action with that of copper, etc., upon nitric acid (§ 159).

188. Uses of Sulphuric Acid. — Sulphuric acid is used in many processes and in *enormous* quantities. We have already learned that it is used in the preparation of *nitroglycerine* (*cf.* § 165), of *nitric acid* (*cf.* § 155), of *hydrochloric acid* (*cf.* § 91), and of *sodium carbonate* by the Le Blanc process (*cf.* § 92). Sulphuric acid is used also in the *refining of petroleum*, to change starch into *glucose*, and to convert the calcium phosphate of bone ash and of phosphate rocks into *soluble* form for use as fertilizers.

No wonder that, as is often stated, "the progress of civilization is proportional to the quantity of sulphuric acid used."

189. Sulphates. — The salts of sulphuric acid may be produced in the usual ways, viz., by neutralizing hydroxides with sulphuric acid, or by dissolving metallic oxides, metallic carbonates, or the metals themselves in the acid.

The following equations represent some of these reactions:

$2\ NaOH + H_2SO_4 = Na_2SO_4 + 2\ H_2O.$
$ZnCO_3 + \text{(dilute)}\ H_2SO_4 = ZnSO_4 + H_2CO_3.$
$Mg + \text{(dilute)}\ H_2SO_4 = MgSO_4 + H_2.$

Sulphates may also be formed by heating chlorides, nitrates, acetates, etc., with concentrated sulphuric acid (*cf.* §§ 91 and 155).

A sulphate that is difficultly soluble in water may be formed by adding dilute sulphuric acid or a *soluble* sulphate to a solution of some salt of the metal. Thus, *strontium sulphate*, $SrSO_4$, is precipitated when dilute sulphuric acid is added to a solution of strontium chloride.

$$SrCl_2 + H_2SO_4 = \mathit{SrSO_4} + 2\ HCl.$$

Test. — We usually *test* an unknown soluble substance to see if it is a sulphate by adding to its solution barium chloride solution or barium nitrate solution; the precipitate of barium sulphate which is formed if a sulphate is present, is *insoluble in acids*.

Thus, $BaCl_2 + Na_2SO_4 = \mathit{BaSO_4} + 2\ NaCl.$

190. Sulphur Trioxide. — *Four* oxides of sulphur are known; but only the *trioxide* (SO_3) and the dioxide (SO_2) need be considered here. Sulphur trioxide is a white, crystalline solid, melting at 15° C. and very soluble in water. When it is brought in contact with water there is a hissing noise, and much heat is liberated. The product of the union is *sulphuric acid.*

$$SO_3 + H_2O = H_2SO_4.$$

Sulphur trioxide is thus the *anhydride* of sulphuric acid.

Sulphur trioxide is produced by the oxidation of sulphur dioxide; a small amount is, therefore, formed when sulphur is burned in air or in oxygen. It is formed in quantity by passing a mixture of dry sulphur dioxide and oxygen over heated platinum sponge or platinized asbestos.

When sulphur trioxide is heated considerably, it breaks up in part into sulphur dioxide and oxygen.

191. Sulphur Dioxide. — Sulphur dioxide is the gas of well-known odor produced by burning sulphur in air or in oxygen. Commercially it is usually formed by *roasting* sulphides, *e. g.*, iron pyrites, in air (*cf.* §§ 178 and 184). The reaction is represented by the equation,

$$\begin{array}{ccccccc} 2\,FeS_2 & + & 11\,O & = & Fe_2O_3 & + & 4\,SO_2. \\ 240 & & 176 & & 160 & & 256 \end{array}$$

From its power of striking sparks with flint, iron pyrites derived its name ; "pyrites" means "firestone."

The method commonly employed for producing sulphur dioxide in the laboratory, viz., by the reduction of concentrated sulphuric acid with copper, has already been considered (*cf.* § 187).

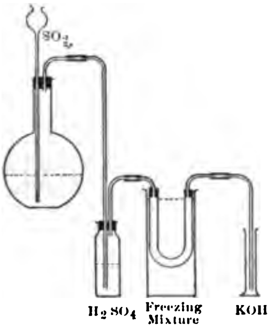


FIG. 42.

Sulphur dioxide is a colorless gas about 2.2 times as heavy as air. One liter of it weighs, at standard conditions, 2.86 grams. The gas is very soluble in water, 80 c.c. of it being absorbed by 1 c.c. of water at 0° C. When the solution is heated the gas is expelled.

Sulphur dioxide may be obtained in liquid form (Fig. 42) by passing it through a condensing tube (conveniently in U form) surrounded by a freezing mixture of ice and salt. The resulting liquid is colorless; it boils at —8° C. The evaporation of liquid sulphur dioxide absorbs much heat; hence this substance is often used as a refrigerating agent.

192. Chemical Properties of Sulphur Dioxide. — An aqueous solution of sulphur dioxide is oxidized *slowly* in the air to sulphuric acid; the oxidation is much more rapid if oxidizing agents are used.

The technical preparation of sulphuric acid by the oxidation of sulphur dioxide by nitric acid has been described already (*cf.* § 184). Other oxidizing agents act in the same way.

Thus, solutions of potassium chromate, bichromate, permanganate, etc., are all *reduced* by sulphur dioxide. The latter is converted by the abstracted oxygen into sulphuric acid.

The chief use of sulphur dioxide, aside from its being the source of sulphuric acid, is as a bleaching agent of silks, woolens, straws, laces, etc., which would be injured by chlorine (*cf.* § 88).

The sulphur dioxide probably unites with the coloring matter of these fabrics, forming colorless compounds. The bleaching effect disappears after a time, however; hence fabrics bleached by sulphur "yellow" with age. Dilute sulphuric acid, also, restores the color of many articles that have been bleached by sulphur dioxide; it probably breaks up the colorless compounds that were formed.

Sulphur dioxide is used also as a disinfectant.

193. Sulphurous Acid. — A solution of sulphur dioxide in water has the properties of a weak acid, and is called sulphurous acid, H_2SO_3. Sulphur dioxide is, therefore, *sulphurous anhydride.* The free acid has not been isolated (*cf.* § 149).

When sulphurous acid is neutralized by the solution of a base, and the solution is evaporated, a *sulphite* is obtained. The same result follows when sulphur dioxide gas is passed into the solution of an alkali.

As in the case of sulphuric acid, two sets of salts exist. Thus, if an exactly sufficient amount of sulphur dioxide is used with sodium hydroxide, the product is sodium sulphite, Na_2SO_3 The equation is, —

$$2\ NaOH + H_2SO_3 \longrightarrow Na_2SO_3 + 2\ H_2O.$$

If, however, sulphur dioxide is passed into sodium hydroxide solution until no more gas is absorbed, the solution contains *sodium hydrogen sulphite*, $NaHSO_3$. The equation is, —

$$NaOH + H_2SO_3 \longrightarrow NaHSO_3 + H_2O.$$

Similar reactions take place with other bases.

Both normal and acid sulphites are decomposed by dilute sulphuric acid and by hydrochloric acid, giving sulphur dioxide. Thus, sodium sulphite and hydrochloric acid react according to the equation,

$$Na_2SO_3 + 2\ HCl = 2\ NaCl + H_2SO_3\ (i.e.,\ SO_2 + H_2O).$$

With sodium hydrogen sulphite the equation is,

$$NaHSO_3 + HCl = NaCl + H_2SO_3\ (i.e.,\ SO_2 + H_2O).$$

By this reaction a *sulphite* may readily be distinguished from a *sulphate.*

Sulphites, like sulphurous acid, oxidize readily in the air.

194. Thiosulphates. — *Thiosulphuric acid,* $H_2S_2O_3$, is sulphuric acid with one-fourth of its oxygen replaced by sulphur ("thion" = sulphur); its salts are called *thiosulphates.*

The most important thiosulphate is the sodium salt, $Na_2S_2O_3$. This is made by boiling a solution of sodium sulphite with sulphur.

$$Na_2SO_3 + S = Na_2S_2O_3.$$

This reaction corresponds to the oxidation of sulphites to sulphates (*cf.* § 193).

When sodium thiosulphate is treated with dilute acids, it breaks down as represented by the equation,

$$Na_2S_2O_3 + 2\ HCl = 2\ NaCl + H_2SO_3 + S.$$

It decomposes, therefore, like a sulphite *plus* sulphur.

Sodium thiosulphate is a reducing agent capable of converting *chlorine* and *iodine* into ***hydrochloric*** and *hydriodic acids,* respectively. It is therefore used to destroy the excess of chlorine in the process of bleaching. It has the power to dissolve silver chloride, bromide, iodide, etc., and is therefore used in "fixing" negatives in photography. Its technical name is "hypo," from its *old* chemical name, "hyposulphite of soda."

195. Exercises.

1. Calculate the per cent of sulphur in galena. In iron pyrites.

2. How many grams of sulphur dioxide can be produced by burning 75 grams of sulphur? How many liters at 20° C. and 740 mm.?

3. How many grams of ferrous sulphide are required to give, with an excess of dilute sulphuric acid, 25 grams hydrogen sulphide? How much ferrous sulphate will be formed?

4. To a solution containing an unknown quantity of sulphuric acid, an *excess* of barium chloride solution was added; the resulting barium sulphate weighed 2.653 grams. How much sulphuric acid was there in the solution?

5. At least how many grams of barium chloride crystals, $BaCl_2 . 2 H_2O$, are required to produce a solution that will precipitate all the sulphuric acid formed when 10 grams of sulphur are dissolved in *fuming* nitric acid?

6. How could you distinguish between sodium sulphite and sodium sulphate?

7. How could you distinguish between sodium chloride and ammonium chloride?

8. How could you distinguish between a soluble sulphide, sulphite, and sulphate?

9. From what you have already learned of ammonium compounds, tell what will probably happen when you heat ammonium sulphide, $(NH_4)_2S$?

CHAPTER XIV.

CARBON AND ITS COMPOUNDS.

196. Carbon. — The element carbon is found in a free and an almost pure state as *diamond*, *graphite*, and *anthracite coal;* it is found *combined* in all *organic* substances, in *carbon dioxide*, in *carbonates*, in *coal*, and in *petroleum.*

Like sulphur, carbon exists in several *allotropic forms* (*cf.* § 175), the forms usually distinguished being (1) diamond, (2) graphite, and (3) amorphous, i. e., *non-crystalline*, carbon.

These three modifications of carbon differ to such an extent that they were long considered different chemical individuals. Their identity is proved by burning them in oxygen; for equal parts by weight of each give equal amounts of carbon dioxide.

$$\underset{12}{C} + \underset{32}{O_2} = \underset{44}{CO_2}.$$

197. The Diamond. — The diamond is prized for its luster, its strong refractive power, and its hardness. It is one of the hardest substances known.

The specific gravity of the diamond is 3.5. Acids and alkalies have practically no effect upon it; but when it is heated to about 700° C. in oxygen, it *burns*, forming carbon dioxide. When a diamond is heated between the poles of a powerful battery it is changed into graphite.

Diamonds have been made artificially by crystallizing carbon *from solution in melted iron.* This process usually gives graphite, but if the melted iron cools under *great pressure* the carbon appears in the form of small diamonds. The necessary pressure is secured by chilling the exterior of the mass of iron: the contraction of the exterior thus causes great pressure upon the interior of the mass.

So far as known, no artificial diamonds yet made are large enough to have any commercial importance.

198. Graphite. — Graphite is sometimes found crystallized, but usually in an amorphous form. Its specific gravity is about 2.25. It owes its name, "black lead," to a confusion of names.

Graphite is a good conductor of heat and of electricity. Owing to its *friability* it is used to make "lead" pencils. Mixed with clay it is the material of graphite crucibles, which are used in making "crucible" steel. Other uses are: To protect iron from the air, as in stove polish, to coat grains of shot, and as a lubricant.

Graphite is produced artificially (*cf.* § 197) by crystallizing charcoal from molten iron and steel.

199. Amorphous Carbon. — The amorphous forms of carbon include the several varieties of coal, gas carbon, coke, charcoal, and lampblack; all of these are formed by the *charring*, i. e., carbonization, of animal or vegetable substances.

200. Natural Carbonization; Coal. — Carbonization has taken place in nature on a large scale. Vegetable matter, accumulated in certain localities through many generations, and decaying in the absence of air, was without doubt the material from which coal was formed. This partially decayed matter was probably much like *peat.* When the peat was buried under sediments, and thus subjected to water and pressure, a slow carbonization took place; as a result gaseous products, such as natural gas, etc., passed off, and the *excess* of carbon remained behind.

The varieties of coal owe their origin to the different degrees of water-action and pressure to which the peat was subjected. Thus, soft, *i. e.*, bituminous, coal contains many gaseous substances, as is shown by its burning with a large flame and much smoke; anthracite coal, on the contrary, is nearly pure carbon, and burns with a *small* flame.

The table on the following page shows the *approximate* composition of wood and of several varieties of coal. The difference between the sum of the parts per cent and 100 represents in each case the *ash,* or mineral matter, of the coal.

201. Artificial Amorphous Carbon. — The artificial carbonization of wood produces *wood charcoal* and *lampblack;* that of soft coal, *coke* and *gas carbon;* that of animal matter (bones, blood, etc.), *animal charcoal* and *bone-black.*

	PER CENT OF			
	CARBON.	HYDROGEN.	OXYGEN.	NITROGEN.
Wood.	50	6.0	43	
Peat.	62	5.7	32	
Lignite.	68	5.7	25	About 1.
Bituminous.	79	5.3	14	About 1.
Cannel.	83	7.0	9	About 1.
Anthracite.	92	3.5	3	About 1.

Lampblack. — Lampblack, or *soot*, is produced by burning resinous wood, or, for the better grades, oil or gas, in an insufficient supply of air. It is used in making printer's ink, black paints, India ink, etc.

Wood Charcoal. — Wood charcoal is made by the "destructive distillation" of wood. The operation may be carried out either in iron retorts, or by piling the wood in heaps covered with sod (Fig. 43) and then setting fire to the heaps. In the latter case *some* of the wood burns, but its combustion gives heat for the decomposition of the remainder.

The charcoal obtained from a given mass of wood weighs from 15% to 25% as much as the wood taken; the loss is due to the escape of volatile substances. The gaseous products were formerly used as illuminating gas; the liquid parts consist of wood spirit (methyl alcohol), acetic acid, etc.

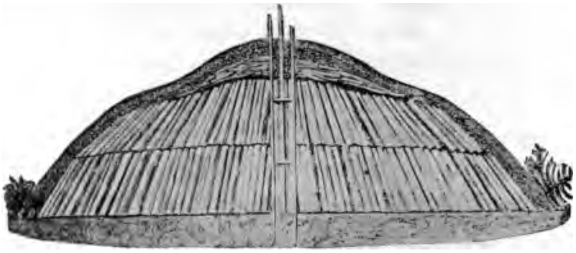


FIG. 43.

Wood charcoal is used in the reduction of iron from its ores and as a disinfectant. It absorbs large quantities of certain gases: ninety volumes of ammonia or nine volumes of oxygen are known to have been taken up by one volume of box-wood charcoal. Charcoal owes its action as a disinfectant to its power of absorbing noxious gases, along with oxygen, in its pores. The oxygen destroys the bacteria in the other gases.

Coke and Gas-Carbon. — *Coke* is the residue left when soft coal is distilled; *gas-carbon* is the volatile coke condensed upon the walls of the retorts.

Gas-carbon is *metallic* in character and a good conductor of electricity; it is used for the negative plates of electric cells and for the pencils of electric arc-lamps.

Coke is used chiefly in metallurgy to reduce the metals from their ores. It is also a fuel.

The volatile products obtained in the distillation of coal consist of illuminating gas, coal-tar (the source of many organic compounds), ammonia, etc. (*cf.* § 143).

Animal Charcoal and Bone-black. — Animal charcoal and bone-black are used to destroy organic coloring matter. When a solution of brown sugar, for example, is filtered through bone-black, the solution becomes colorless. Vinegar may be clarified in the same way.

When bones are distilled destructively the volatile products consist largely of *bone-oil.* Usually the bones are deprived of their gelatine before being carbonized. In either case the animal charcoal obtained contains the mineral matter of the bones.

202. Carbon Dioxide; Occurrence. — There are two compounds of carbon and oxygen, viz., *carbon monoxide* and *carbon dioxide;* of these the latter is by far the more important.

Carbon dioxide is present in the air, in some mineral springs, and in certain localities where it escapes from the earth. Ten thousand parts by volume of air contain, on the average, about 3.5 parts of carbon dioxide (*cf.* § 117).

Carbon Dioxide Exhalations. — At Herste, near Driburg, Germany, certain borings made in 1894 struck carbon dioxide at a depth of 148.5 meters. A violent outburst of the gas took place, no less than 40,000,000 liters escaping daily. The carbon dioxide was 99.84% pure. In 1897, 10,000 kilograms, *i.e.*, about one-eighth of the outflow, were liquefied daily.

The origin of the carbon dioxide was probably the action of certain silicates, *i. e.*, salts of *silicic acid*, H_2SiO_3, upon calcium carbonate.

203. Preparation of Carbon Dioxide. — In the laboratory, carbon dioxide is commonly made by decomposing a carbonate by an acid. The carbonate generally used is *marble*, $CaCO_3$. The reaction of marble with hydrochloric acid is represented by the equation,

$$CaCO_3 + 2\ HCl = CaCl_2 + H_2CO_3\ (\textit{i. e.}, CO_2 + H_2O).$$

Evaporation of the solution, after all action ceases, gives calcium chloride, $CaCl_2$, the substance used to dry gases, etc.

204. Physical Properties. — Carbon dioxide is a colorless gas. It has the slightly acid taste known to all who drink "soda water." It is about one and one-half times as heavy as air; one liter weighs 1.97 grams at standard conditions.

Gaseous carbon dioxide may be condensed to the liquid state at *ordinary* temperatures by a pressure of about fifty atmospheres; above 31° C., however, — its critical temperature, — the gas cannot be liquefied by pressure. If liquid carbon dioxide is allowed to evaporate rapidly, it solidifies, forming a white mass like snow. When liquid air (*cf.* § 122) evaporates, solid carbon dioxide is usually left behind.

About ten million kilograms of liquid carbon dioxide are used annually.

Water absorbs about 1.8 times its own volume of carbon dioxide gas at standard conditions; with increase of pressure the amount dissolved *increases.* When the excess of pressure is removed from water *surcharged* with carbon dioxide, much carbon dioxide escapes; hence the sparkling of "soda water" and also of spring water, which usually has carbon dioxide in solution.

205. Chemical Properties. — Carbon dioxide does not allow ordinary burning to continue in it any more than water does, and for the same reason.

Because of its inability to support combustion, carbon dioxide is used to extinguish fires. For this purpose it is generated in a strong reservoir by the action of dilute sulphuric acid upon sodium carbonate.

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2CO_3 \ (i.e.,\ H_2O + CO_2).$$

The resulting gas is directed in a stream upon the flames.

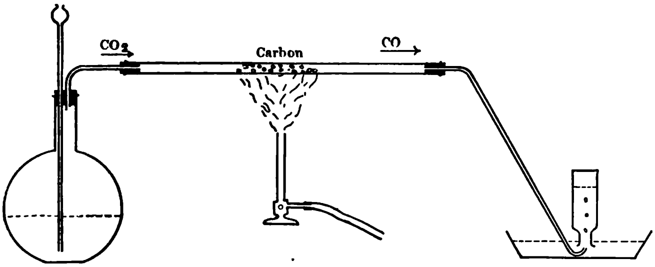


FIG. 44.

Very *strongly* burning substances, however, continue to burn in the gas; examples are *sodium* and *magnesium.*

The equations for the action of burning sodium upon carbon dioxide are, —

$$(1)\ 4\,Na + CO_2 = 2\,Na_2O + C.$$
$$(2)\ Na_2O + CO_2 = Na_2CO_3.$$

When carbon dioxide is passed over red-hot carbon (Fig. 44) it is reduced to carbon monoxide (*cf.* § 212).

$$CO_2 + C \longrightarrow 2\,CO.$$

The *volume* of the carbon dioxide formed by the union of a given volume of oxygen with carbon *is equal to the volume of the oxygen.*

$$\begin{array}{ccc} C + & O_2 = & CO_2. \\ 12 & 32 & 44 \\ & 1\text{ vol.} & 1\text{ vol.} \end{array}$$

Of the volume of the carbon nothing can be stated, because carbon cannot readily be obtained in the gaseous state.

206. Other Sources and Uses of Carbon Dioxide. —

FIG. 45.

(*a*) **Fermentation.** When an aqueous solution of cane sugar or grape sugar is subjected to the action of the yeast plant, the sugar is decomposed; the chief products are *ethyl alcohol*, C_2H_5OH, and carbon dioxide. The alcohol remains in solution, but most of the carbon dioxide escapes in gaseous form.

Fig. 45 shows some characteristic yeast plants in the process of budding.

The decomposition of sugar by yeast is called *alcoholic fermentation.* Grape sugar is a complex compound of the formula $C_6H_{12}O_6$; its decomposition in fermentation is *chiefly* according to the equation,

$$C_6H_{12}O_6 = 2\,CO_2 + 2\,C_2H_5OH.$$

The brewer uses fermentation to produce alcoholic liquors; the baker, to *raise* bread.

(*b*) **Baking Powders.** Ordinary baking powder is a mixture of *potassium hydrogen tartrate*, $KHC_4H_4O_6$ (commonly called "cream of tartar"), and *sodium bicarbonate*, $NaHCO_3$, with some diluting substance, *e. g.* corn-starch. The ingredients act upon each other only when moist or in solution. The equation for the decomposition of baking powder is, —

$$KHC_4H_4O_6 + NaHCO_3 = KNaC_4H_4O_6 + H_2CO_3.$$

The substance $KNaC_4H_4O_6$ is called "Rochelle Salt."

Theoretically, any substance that will liberate carbon dioxide from sodium bicarbonate might be used in place of cream of tartar, but practically a substance must be used that will not form a residue injurious to the human system.

"Acid Phosphate" baking powders contain sodium bicarbonate and *calcium hydrogen phosphate*, $CaH_4(PO_4)_2$. The calcium hydrogen phosphate liberates carbon dioxide from sodium bicarbonate, just as cream of tartar does.

207. Relation of Carbon Dioxide to Life. — Substances containing carbon usually give by their oxidation carbon dioxide. The same result follows whether the oxidation is slow or rapid. Hence all *decay*, as of wood, paper, etc., results in the formation of this gas.

Carbon dioxide fails to support animal life, not because carbon dioxide is *poisonous*, but because animals cannot extract from it the oxygen necessary for respiration. Besides, the presence of even a little more than the normal amount of carbon dioxide in the air, say, 7 or 8 parts in 10,000, prevents the proper exit of carbon dioxide from the lungs.

The fact that the enormous quantity of carbon dioxide constantly poured into the air by the respiration of animals and plants does not accumulate until it destroys higher animal life is due largely to the agency of vegetation.

To plants, carbon dioxide is an important *food;* for chlorophyll-producing, i. e., *green*, plants are able to convert carbon dioxide and water, *in the presence of light*, into sugar, starch, wood, and the various compounds of carbon, hydrogen, and oxygen of which most vegetable products consist.

The natural *cycle* through which carbon dioxide passes is impressive : —

(1) Plants, by means of energy derived from the sun, change carbon dioxide and water into plant tissue;

(2) Animals, appropriating the stored-up energy of plants, give it forth in their activities and return carbon dioxide to the air.

208. Carbonic Acid. — The aqueous solution of carbon dioxide has slightly acid properties and gives *carbonates* with soluble bases; hence the substance H_2CO_3 — *carbonic acid* — probably exists in solution. Carbon dioxide is thus *carbonic anhydride.*

Carbonic acid cannot be isolated; for it breaks up very readily into carbon dioxide and water.

$$H_2CO_3 = H_2O + CO_2.$$

In its instability carbonic acid is like ammonium hydroxide and sulphurous acid (*cf.* §§ 149 and 193).

209. Carbonates. — When carbon dioxide is passed into solutions of metallic hydroxides it is absorbed, forming *carbonates.*

Thus, sodium hydroxide and carbonic acid (carbon dioxide with water is probably *carbonic acid*) react according to the equation,

$$2\ NaOH + H_2CO_3\ (i.\ e., CO_2 + H_2O) = Na_2CO_3 + 2\ H_2O.$$

A similar reaction takes place when carbon dioxide is passed into a solution of calcium hydroxide (lime-water); but in this case the carbonate formed is *insoluble.* As a result the lime-water becomes "milky."

The equation is, —

$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2\ H_2O.$$

With *baryta-water* (barium hydroxide solution) the result is analogous.

$$Ba(OH)_2 + H_2CO_3 = BaCO_3 + 2\ H_2O.$$

If a gas forms a white precipitate on being passed into lime-water or baryta-water, we generally assume that *the gas is carbon dioxide* (*cf.* § 117).

All the common carbonates except those of sodium, potassium, and ammonium are *insoluble* in pure water, and are, therefore, *precipitated* when one of the three soluble carbonates is added to the solution of a metal salt.

Thus, *sodium carbonate* gives with *calcium chloride* a precipitate of *calcium carbonate.*

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2\ NaCl.$$

Most carbonates except those of sodium and potassium decompose, when heated, into the corresponding oxides and carbon dioxide.

Thus, marble gives, when heated, quicklime and carbon dioxide.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Ammonium carbonate is, of course, decomposed by heat, like other ammonium salts. It is often called "*sal volatile.*"

The common method of *identifying* a carbonate is to treat it with a dilute acid and then to prove that the escaping gas is carbon dioxide.

210. Bicarbonates. — If carbon dioxide is passed into lime-water long enough, the precipitate of calcium carbonate, which is formed at first, will be *redissolved*. A similar result takes place with barium hydroxide. This phenomenon may be best understood by comparing it with the action of carbonic acid (*i. e.*, carbon dioxide and water) upon sodium carbonate — a reaction represented by the equation,

$$Na_2CO_3 + H_2CO_3 \text{ (i. e., } CO_2 + H_2O) \longrightarrow 2\ NaHCO_3.$$

The substance $NaHCO_3$ is *sodium hydrogen carbonate* (called, also, sodium bicarbonate): when it is heated gently it breaks up into sodium carbonate, carbon dioxide, and water.

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + H_2CO_3 \text{ (i. e., } H_2O + CO_2).$$

In a similar way an excess of carbonic acid converts calcium carbonate into *calcium hydrogen carbonate*, $Ca(HCO_3)_2$. The precipitate of calcium carbonate redissolves, therefore, owing to the formation of *calcium bicarbonate*, which is soluble. The equation is, —

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2.$$

Calcium bicarbonate is, however, *very unstable*; it decomposes, when its solution is heated, into calcium carbonate, carbon dioxide, and water. *Hence the precipitate of calcium carbonate reappears on boiling.*

The behavior of calcium carbonate with an excess of carbon dioxide explains the solubility of limestone in natural waters which contain this gas; and the ease with which calcium bicarbonate is decomposed explains why most waters deposit their limestone upon the walls of vessels in which they are heated (*cf.* § 40).

In many limestone regions underground waters are charged under pressure with carbon dioxide, and therefore take up large quantities of limestone; subsequently the carbon dioxide escapes, and the limestone is deposited. These limestone deposits often take on beautiful and fantastic forms, as *stalactites*, etc. See Fig. 46.

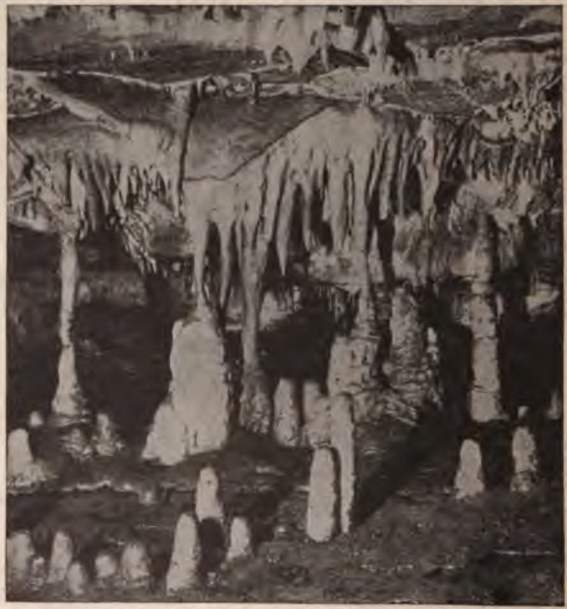


FIG. 46.
CAVE AT MARENGO, INDIANA.

211. **Natural Carbonates.** — The most abundant natural carbonate is *limestone*, $CaCO_3$. Large quan-

tities of this substance are distributed over the land and in the sea.

Marble is a finely crystallized limestone. *Iceland spar* is almost pure calcium carbonate; it occurs in large crystals. *Coral* is limestone taken from the sea by the coral polyp and left as a residue when the polyp dies. The *shells* of most water animals are largely limestone.

A natural mixture of calcium and magnesium carbonates called ***dolomite*** is also very abundant; it is the chief component of whole ranges of the Alps mountains. ***Magnesite*** is natural magnesium carbonate.

Sodium carbonate and ***potassium carbonate*** exist in the soil of many places. The ashes of sea-plants contain sodium carbonate; those of land-plants, potassium carbonate.

Both of these carbonates are used in large quantities and are made ***synthetically***, especially sodium carbonate, on an enormous scale (*cf.* § 92). A large and valuable deposit of almost pure sodium carbonate occurs at Owen's Lake, California.

212. Formation of Carbon Monoxide. — Carbon monoxide is produced by the reduction of carbon dioxide by hot carbon. This operation is illustrated in Fig. 44. The equation is, —

$$CO_2 + C \longrightarrow 2\,CO.$$

A common illustration of the same reaction is seen in every coal fire. The coal at the bottom (Fig. 47) burns to carbon dioxide; but as this gas passes through the bed of heated coal prepared by heating *mercuric cyanide*, $Hg(CN)_2$, or silver cyanide, $AgCN$.

With silver cyanide the equation is, –

$$2\ AgCN = 2\ Ag + C_2N_2.$$

A cheaper way is to allow a solution of *potassium cyanide*, KCN, to fall drop by drop into a hot solution of cupric sulphate. *Cupric cyanide*, $Cu(CN)_2$, is first formed, but at once breaks up into *cuprous cyanide*, $Cu_2(CN)_2$, and cyanogen.

$$(1)\quad CuSO_4 + 2\ KCN = Cu(CN)_2 + K_2SO_4.$$

$$(2)\quad 2\ Cu(CN)_2 = Cu_2(CN)_2 + C_2N_2.$$

Cyanogen is a colorless, sweet-smelling gas. It burns with a beautiful, lavender-colored flame, forming carbon dioxide and nitrogen.

$$C_2N_2 + 2\ O_2 = 2\ CO_2 + N_2.$$

The flame of cyanogen is *double*, i. e., it has *two* zones of combustion (*cf.* §§ 11 and 214).

Cyanogen is *so poisonous* that no one but an experienced person should make it in quantity, and then only where there is a *strong draught.*

216. Hydrocyanic Acid. — Hydrocyanic, or *prussic*, acid is extremely poisonous. It may be made by treating *cyanides*, e. g., potassium cyanide or potassium ferrocyanide, with dilute sulphuric acid.

$$KCN + H_2SO_4 = KHSO_4 + HCN.$$

It is a colorless, sweet-smelling liquid, boiling at 27° C.

217. Compounds of Carbon and Hydrogen. — The number of compounds formed by carbon and hydrogen is very large. At present we shall consider only *four*, viz.: *methane*, CH_4; *ethane*, C_2H_6; *ethylene*, C_2H_4, and *acetylene*, C_2H_2. All are colorless gases.

218. Methane. — Methane, or *marsh gas*, is formed in the destructive distillation of coal, and is therefore present in illuminating gas made by the old process (*cf.* § 223). It is formed in nature by the decay of organic matter, *e. g.*, leaves, twigs, etc., under water; hence the name "marsh gas." The presence of the gas may be observed by disturbing the material at the bottom of most stagnant pools, especially in summer.

Marsh gas also enters coal mines; here its mixture with air forms the dreaded "*fire damp*" (damp = gas; *cf.* Ger. Dampf.), which explodes with frightful violence when ignited. It was to avoid these explosions in mines that Davy made his celebrated "safety lamp" (*cf.* § 32).

Methane forms over ninety per cent of the gases that escape from petroleum wells.

Marsh gas is commonly made in the laboratory by heating a mixture of *sodium acetate*, $NaC_2H_3O_2$, *sodium hydroxide*, and *quicklime*. The gas thus produced is not pure, however; it contains *hydrogen* and other impurities. An *approximate* equation is,

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

The equation representing the combustion of marsh gas is, —

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O.$$

1 vol. 2 vols. 1 vol. 2 vols. (steam)

219. Ethane. — Ethane is formed along with marsh gas in the decomposition of many organic substances, and is a constituent of illuminating gas. Its composition is represented by the formula, C_2H_6. It burns with an almost colorless flame.

In burning, ethane produces carbon dioxide and water, just as marsh gas does, but the relative proportions are different. This fact is shown by the equation,

$$2\ C_2H_6 + 7\ O_2 = 4\ CO_2 + 6\ H_2O.$$

2 vols. 7 vols. 4 vols. 6 vols. (steam)

220. Ethylene. — Ethylene may be prepared by heating ethyl alcohol, C_2H_5OH, with concentrated sulphuric acid to above 140° C. The following equation represents *in part* what takes place: —

$$C_2H_5OH - H_2O = C_2H_4.$$

Ethylene is present in illuminating gas; it burns with a bright, *luminous* flame, producing carbon dioxide and water.

$$C_2H_4 + 3\ O_2 = 2\ CO_2 + 2\ H_2O.$$

1 vol. 3 vols. 2 vols. 2 vols.

The most remarkable property of ethylene is its power to absorb chlorine and bromine, giving ethylene chloride and bromide.

Thus, $C_2H_4 + 2\,Br = C_2H_4Br_2$.
$\qquad 28 \qquad 160 \qquad 188$

Both the chloride and the bromide are heavy, colorless oils.

221. Acetylene. — Like the other compounds of hydrogen and carbon that have been mentioned, acetylene is present in illuminating gas. It is formed when a Bunsen burner burns at the base instead of at the top, and may then be recognized by its penetrating odor.

Acetylene has been formed by passing an electric spark between carbon terminals in a vessel of hydrogen.

$$2\,C + H_2 = C_2H_2.$$

Acetylene has recently been made on a commercial scale by the action of water containing a little hydrochloric acid upon the *carbides* of certain metals. The carbide commonly used is *calcium carbide*, CaC_2. The decomposition of this substance by water is represented by the equation,

$$CaC_2 + 2\,H_2O = C_2H_2 + Ca(OH)_2.$$

Calcium carbide is produced by heating a mixture of *quicklime*, CaO, and coal, or coke, in the *electric furnace*. The reaction is represented thus: —

$$CaO + 3\,C = CaC_2 + CO.$$

A section of a simple electric furnace is shown in Fig. 48.

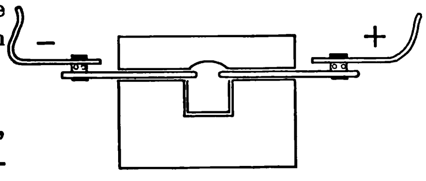


FIG. 48.

Acetylene burns, under proper conditions, with a flame of dazzling whiteness and without soot. It is readily condensed to the liquid state. Ordinary mixtures of gaseous acetylene and air are very explosive.

The equation for the combustion of acetylene is, —

$$\underset{2\text{ vols.}}{2\,C_2H_2} + \underset{5\text{ vols.}}{5\,O_2} = \underset{4\text{ vols.}}{4\,CO_2} + \underset{2\text{ vols.}}{2\,H_2O}.$$

222. Illuminating Gas. — Illuminating gas is a mixture of several gases already studied. These gases may be divided into (*a*) *combustible* gases and (*b*) *impurities*.

The impurities are chiefly *nitrogen* and *carbon dioxide*.

The combustible gases are of two kinds: —

(1) Those that burn without giving light, and (2) those that burn with luminous flames.

The *non-illuminating* gases are *hydrogen*, *methane*, and *carbon monoxide*; they make up about ninety per cent by volume of the gas. The *illuminating* gases are the so-called "heavy hydrocarbons," *ethane*, *propane*, C_3H_8, *butane*, C_4H_{10}, etc., and, usually, small amounts of *ethylene* and *acetylene*.

Two general processes are employed in making illuminating gas: —

(1) The distillation of soft coal.

(2) The "water-gas" process.

223. Illuminating Gas by Distillation of Coal. — The *old* process of making gas is carried out as shown in Fig. 49.

Soft coal in the retorts C (there are usually several retorts, one over the other) is heated by the fire A to the temperature of decomposition. The volatile products pass off through the pipe T into the "hydraulic main" B. The hydraulic main contains water, which condenses much *tar*, etc., from the gas. From B the gas passes through the "condensers" D, which stand over water; here the gas is cooled, and more of the tarry products are condensed.

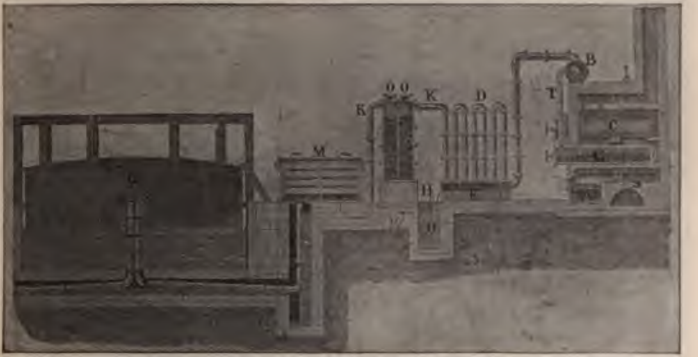


FIG. 49.

From the condensers the gas passes through the coke towers, or "scrubbers" O; into these water is sprayed, and the illuminating gas is thereby freed from *soluble* gases, such as *ammonia* and *hydrogen sulphide*.

From the "scrubbers" the gas passes into the "purifiers" M. The purifiers are large boxes containing trays of slaked lime; this substance removes carbon dioxide and traces of hydrogen sulphide. The gas then enters the gas holder G; thence it is distributed to the community through the service pipe S′.

Many other valuable products besides illuminating gas are obtained by the distillation of coal. The ammoniacal liquors of the condensers and coke towers are the sources of *ammonium* compounds (*cf.* § 143); the tar of the hydraulic main and condensers gives, when distilled, the important substances *benzene*, *toluene*, *phenol* (carbolic acid), *naphthalene*, etc.; the residue in the retorts is *coke* and *gas carbon* (*cf.* § 201).

The composition of a representative illuminating gas made by the old process is shown in the table accompanying § 225.

224. Water-gas Process. — Within recent years the old process for the production of artificial gas has been almost entirely displaced by the "water-gas" process. In this process steam is passed over white-hot anthracite coal. The reactions which take place are represented by the equations,

$$(1)\quad C + 2\,H_2O = CO_2 + 2\,H_2.$$
$$(2)\quad CO_2 + C = 2\,CO.$$

The mixture of carbon monoxide and hydrogen is "water-gas." It may be used directly for fuel, but not for lighting, since it burns with a colorless flame.

For the conversion of water-gas into an illuminating gas, the water-gas is "enriched" by the addition of petroleum hydrocarbons. The process of making an illuminating water-gas will be understood from Fig. 50.

Anthracite coal is heated to white heat in the "generator" by means of a blast of air forced through the coal by the engine. The blast of air is then cut off, and superheated steam is forced over the coal, reacting with it, as already

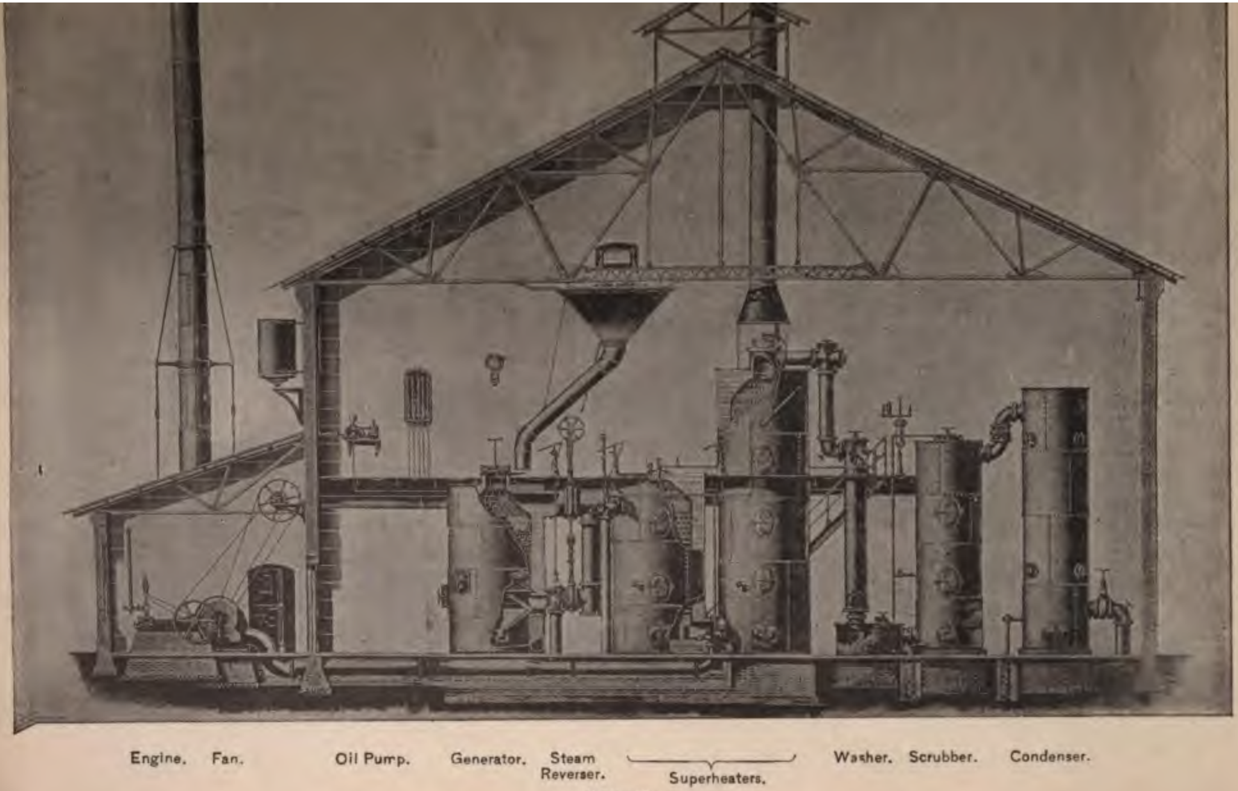


FIG. 50.

DOUBLE SUPERHEATER WATER-GAS APPARATUS.

shown, to form carbon monoxide and hydrogen. The mixture of these two gases is then forced into the "superheaters," in which light petroleum oils are being decomposed by heat. Here the water-gas obtains marsh gas and the hydrocarbons which give ordinary gas its illuminating power.

From the superheaters the gas passes through the "scrubber" and the "condenser," in which the undecomposed petroleum and any carbon dioxide, etc., are removed.

225. Comparison of the Two Kinds of Gas. — The composition of two samples of illuminating gas, one made by the distillation of coal and the other by the "water-gas" process, is given in the following table: —

	OLD PROCESS.	NEW PROCESS.
Hydrogen.	46.0%	29.5%
Methane.	39.0%	20.0%
Carbon monoxide.	5.5%	32.7%
Hydrocarbons.	6.0%	11.2%
Carbon dioxide.	1.2%	2.8%
Oxygen.	0.3%	0.0%
Nitrogen (by difference).	2.0%	3.8%
Total	100.0%	100.0%

Gas made by the "water-gas" process is more poisonous than that made by the distillation of coal, owing to the presence of the large quantity of carbon monoxide in water-gas; otherwise the two gases do not differ greatly in properties.

226. Amount of Gas Used. — The quantity of manufactured gas used in the United States is enormous; it amounts to about sixty thousand millions of cubic feet annually.

The city of Chicago alone used, during the year 1900, not less than seventy-five hundred millions of cubic feet of artificial gas, to say nothing of natural gas.

227. Exercises.

1. How many grams of carbon are needed to reduce 15 grams cupric oxide, CuO, if the carbon is oxidized to carbon dioxide? How many grams of carbon dioxide are formed?

2. What volume of carbon dioxide at 0° C. and 760 mm. can be produced from 840 grams magnesium carbonate, $MgCO_3$?

3. How many grams of sodium bicarbonate are needed to give, *when heated*, 36 liters of carbon dioxide? (*Cf.* § 210.)

4. What is the formula of barium hydrogen carbonate? What products are formed when its solution is boiled?

5. How many liters of carbon dioxide are formed, at standard conditions, by the combustion of 250 grams carbon monoxide?

6. Calculate the percentage composition of calcium carbonate, carbon dioxide, oxalic acid.

7. How would you distinguish between sodium carbonate, sodium sulphite, and sodium sulphide, chemically?

8. How would you distinguish between the gases carbon dioxide, carbon monoxide, oxygen, hydrogen, and ammonia?

CHAPTER XV.

FLAMES. HEAT OF FORMATION AND DECOMPOSITION.

A. Flames.

228. Luminosity of Flames. — As stated in Chapter II, § 33, *a flame is a burning gaseous body.* The amount of light given off by a flame depends upon the *nature* of the burning substance and upon its *density.*

As an illustration of the influence of density, we may take the case of hydrogen. This substance ordinarily burns in air and in oxygen with an almost invisible flame; if, however, the hydrogen and the oxygen are very much compressed before ignition, the flame produced by their union is a very brilliant one.

The illuminating power of all ordinary flames is due to the presence of *incandescent* **solid** *particles.* This may be illustrated by introducing any fine dust into a flame of hydrogen or into the colorless Bunsen flame; the flame at once becomes luminous.

In the combustion of substances containing carbon, — such substances as candles, illuminating gas, paper, petroleum, wood, coal, etc., — the luminosity of the flame is due to the *glowing* of particles of carbon in the flame. A cold object inserted into the flame produced by one of these substances becomes covered with soot; and too little air, or too much air, causes the flame to smoke, owing to the escape of unburned particles of carbon.

229. Structure of Flames. — A burning candle shows practically the same phenomena as the other compounds of carbon just named, and may be taken as representative of them.

The burning of a small portion of the wick of the candle furnishes heat enough to melt some of the wax. The wick then draws the melted wax, by capillary action, into the flame, where the wax is first vaporized and then ignited.

If the candle flame be examined, it will be found to consist of several regions, or *zones*, of combustion, surrounding a central cone-shaped region of unburned gases. These parts are shown in vertical section in Fig. 51.

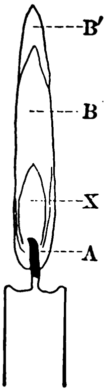


FIG. 51.

X is the region of unburned gases.

B is the luminous zone. It contains solid particles of carbon in a state of combustion. *B'* is the *ruddy* tip of the luminous zone.

A is the outer mantle of the flame. Being non-luminous it is obscured by the light of *B*, except at the bottom, where it forms a blue, cup-shaped region.

In addition to the parts just named, an important region is believed to exist about the region *X*. This zone is designated *C* in the *idealized* section of a candle flame (Fig. 52). Being non-luminous, the region *C* is obscured by the light of *B*.

Whether a flame is to be luminous or non-luminous depends upon the condition of affairs in the region *C*.

What takes place in a candle flame is probably as follows: —

The vaporized paraffin (wax) of the region *X* (Fig. 52) burns in part in the zone *C*, producing enough heat to decompose some of the paraffin vapor into hydrogen, certain hydrocarbons (especially acetylene), and solid carbon. These substances burn further in the region *B*, the carbon burning, as usual, with a bright *glow*, and thus causing the luminosity of this region. In *A* the gases and the carbon escaping unburned through *B* are more or less completely burned.

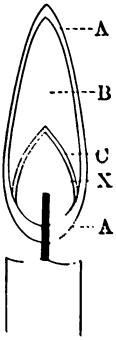


FIG. 52.

230. Non-Luminous Flames. — The decomposition of the combustible material of region *X* (Fig. 52) into acetylene, carbon, etc., in the region *C* requires a *definite degree of temperature;* hence, if the temperature of *C* is sufficiently lowered, the flame becomes non-luminous. This is exactly what takes place in practice; for if large quantities of a cold diluting gas, *e. g.*, air, carbon dioxide, or nitrogen, are introduced into *X*, thus cooling *C*, the luminosity of the flame is destroyed. If, however, the diluting gases are first heated, the non-luminous flame becomes luminous.

In the non-luminous flame the region *C* may readily be distinguished by its light-blue color.

The explanation of non-luminosity in flames, just given, contains the theory of the Bunsen burner (Fig. 53). When the holes at the base of the burner are open, the gas which rushes past the holes draws in currents of air, and the flame is non-luminous; when the holes are closed the flame is luminous. Carbon dioxide, nitrogen, etc., give the same result as air.

The zones of combustion in the *Bunsen* flame are as follows (Fig. 54): —

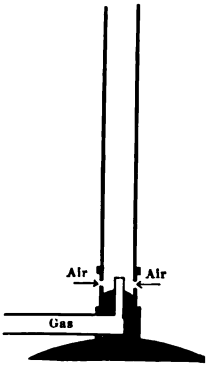


FIG. 53.

X is the region of unburned gas, as in the candle flame.

C is the light-blue, inner cone surrounding *X*.

B is the non-luminous, dark cone. In the candle flame this is luminous.

A is the purple, outer mantle. In the candle this is the faintly luminous *halo* surrounding the flame.

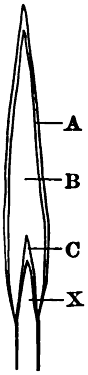


FIG. 54.

231. Simple and Complex Flames. — The *simplest* flames are those having only *one* cone of combustion. Illustrations are the flames of carbon monoxide (*cf.* § 214) and hydrogen (*cf.* § 11). It is to be noted that these are substances that can have only *one* combustion in air; for carbon monoxide can burn only to form carbon dioxide, and hydrogen only to form water.

Substances that can have *two* combustions burn with flames consisting of *two* zones.

The best illustration of this fact would probably be *gaseous carbon*, if it could be obtained. In place of carbon we can use cyanogen, C_2N_2 (*cf.* § 215); for the nitrogen takes practically no part in the combustion. Cyanogen really burns with a flame consisting of two zones. Both carbon and carbon monoxide burn to carbon dioxide in its flame.

The flame of a *hydrocarbon*, in which *three* combustions are possible, has, like that of a candle, **three** regions of combustion.

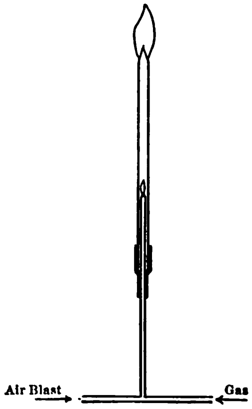


FIG. 55.

232. Dissection of Flames. — Complex flames may be dissected and the separate zones made to burn by themselves. This may be done with illuminating gas as follows: —

Two pieces of glass tubing, one larger in diameter than the other (Fig. 55), are joined by a rubber tube so that the inner tube may be moved within the outer one. At first the inner tube is so adjusted that its top is just below that of the outer tube. The inner tube is connected with an *inverted* T-tube.

Illuminating gas is passed through one arm of the T-tube and lighted at the top of the larger (outer) tube; then a current of air is forced through the other arm of the T. By a careful adjustment of the air supply to that of the gas, the colorless Bunsen flame is obtained.

If, now, while the colorless flame is burning, the inner tube is *lowered*, so that the distance between the tops of the two tubes is gradually *increased*, a position will be found at which the flame divides into *two* flames, one upon the outer tube and one upon the inner tube.

B. Heat of Formation and of Decomposition.

233. Energy Changes Accompany Chemical Changes. — Chemical changes result not only in the formation of new substances, but also in the evolution or the absorption of energy. The energy may appear in the form of heat, light, electric effects, etc.

To illustrate: The union of carbon with oxygen produces carbon dioxide; but at the same time a considerable evolution of heat and light takes place. Since the energy evolved comes from the carbon and the oxygen, carbon dioxide must possess less energy than the elements which produced it. So, also, water has less energy than the hydrogen and oxygen from which it was formed.

A mixture of elements capable of uniting chemically with *evolution* of heat must be looked upon as having **potential energy.** In the act of union this energy is partly given up in the kinetic, i. e., *active*, form; while in the resulting compound there must be *less* energy than existed in the elements. Furthermore, to restore the carbon and the oxygen of carbon dioxide to the elementary condition, as much energy must be *added to* the carbon dioxide as was evolved when the elements united.

234. Heat of Formation and of Decomposition. — The quantity of heat evolved in many cases of chemical action has been determined by experiment. If we call the amount of heat necessary to raise the temperature of one gram of water from 0° C. to 1° C. a *gram-centigrade* (g. c.) heat unit, we may write the equation for the union of hydrogen and oxygen as follows: —

$$H_2 + O = H_2O + 68{,}400 \text{ g. c. heat units.}$$

This equation shows not only that 2 grams of hydrogen and 16 grams of oxygen unite to form 18 grams of water, but also that by their union 68,400 heat units are liberated.

Similarly, for the union of 12 grams of carbon and 32 grams of oxygen we may write, —

$$C + O_2 = CO_2 + 97{,}000 \text{ g. c. heat units.}$$

For the union of 1 gram of hydrogen and 35.5 grams of chlorine the equation is, —

$$H + Cl = HCl + 22{,}000 \text{ g. c. heat units.}$$

The *difference* between the energy (calculated as heat) possessed by the elements which united to form a compound and that possessed by the compound itself is called the **heat of formation** of the compound.

The **heat of decomposition** of a compound is *numerically equal* to the heat of formation; that is to say, the quantity of heat necessary to separate a compound *into* its elements is just as great as that evolved when the compound was formed *from* its elements.

235. Positive and Negative Heat of Formation. — The heat of formation of water, of carbon dioxide, and of hydrochloric acid is positive (+), heat being *evolved* when these compounds are formed; many cases, however, exist in which heat is not evolved, but *absorbed* in the formation of a compound from its elements. In such cases the heat of formation is negative (—).

An illustration is the case of carbon disulphide, a substance which is produced (*cf.* § 183) by passing sulphur vapor over hot charcoal. Carbon burns in sulphur with *absorption* of heat. The quantity of heat rendered *potential* by the union of 12 grams of carbon and 64 grams of sulphur is shown by the equation, —

$$C + 2\,S = CS_2 - 19{,}600 \text{ g. c. heat units.}$$

Similarly, hydrogen and iodine unite with absorption of heat.

$$H + I = HI - 6{,}100 \text{ g. c. heat units.}$$

A compound with a negative heat of formation is in a state of *tension*, or of unstable equilibrium; for it is possessed of more energy than its constituent elements. When such a compound is decomposed, energy is *evolved.*

236. Heat of Formation Evolved in Stages. — Just as it makes no difference in the total quantity of heat given out whether a given mass of a combustible burns slowly or rapidly (*cf.* § 28), so the total amount of heat evolved (or absorbed) in the formation of a compound is the same whether the compound is formed in one or in several stages.

Thus, the heat of formation of *calcium carbonate*, $CaCO_3$, is equal to the sum of the heats of formation of *calcium oxide*, CaO, and of *carbon dioxide*, CO_2, *plus* the heat evolved when calcium oxide and carbon dioxide unite to form calcium carbonate.

CHAPTER XVI.

MOLECULES AND ATOMS.

237. Law of Multiple Proportions. — We have already learned (*cf.* § 69) that chemical changes take place between definite masses of substances, and that any given chemical compound always contains the same elements united in the same proportion. While there is no reason to doubt these statements, a further fact is also true, and has already been stated, viz., that the same two (or more) elements may unite in *different* proportions to form *different compounds.*

Thus, carbon and oxygen unite in the proportion of 3 parts of carbon to 4 of oxygen to form carbon *mon*oxide, and in the proportion of 3 of carbon to 8 of oxygen to form carbon *di*oxide. Similarly, iron and sulphur form *three* distinct compounds; sulphur and oxygen, *two* or more (*cf.* § 190); nitrogen and oxygen, *five* (*cf.* §§ 166 to 171); potassium, chlorine, and oxygen, *four* (potassium salts of the chlorine acids named in § 106).

All of the cases named illustrate the **Law of Multiple Proportions**, which may be stated in its simplest form as follows: —

If two elements form several compounds with each other, the different masses of one element which combine with a fixed mass of the other bear a simple ratio to one another.

Thus, as stated above, the ratio between the *two* quantities of oxygen combining with 3 parts of carbon is 4:8, *i. e.*, 1:2. The ratio between the *two* quantities of oxygen combined with 2 parts of sulphur in sulphur *di*oxide and sulphur *tri*oxide is 2:3; that between the five quantities of oxygen combined with 7 parts of nitrogen is 8:16:24:32:40, *i. e.*, 1:2:3:4:5.

The law of multiple proportions was stated by John Dalton, in 1804, from the consideration of only a *few* compounds; but it has been confirmed by the work of the past century, and is one of the fundamental principles of Chemistry.

238. The Atomic Hypothesis. — We may regard matter as made up in either of two ways: (1) as infinitely divisible, or (2) as composed of small, *indivisible* particles. We know that a piece of gold, for example, can be divided into very small pieces; and we may imagine that the subdivision of the gold might be continued forever. On the other hand, we may suppose that after repeated subdivision the particles of gold become so small that they cannot be divided further.

Both of these views of matter may be reasoned about, but cannot be proved. The hypothesis that matter is composed of indivisible particles is generally known as the **atomic** hypothesis, or theory. The indivisible particles are called **atoms,** from the Greek *atomos*, meaning "indivisible." At the present time chemists usually hold the atomic hypothesis.

239. The Law of Definite Proportions Explained by the Atomic Theory. — Dalton saw that the idea of indivisible particles was connected with the laws of definite and multiple proportions. For, if elements are made up of atoms, all the atoms of any one element will probably have the *same* mass; while atoms of different elements will have *different* masses. When, therefore, two elements unite, the union must take place between the *atoms* of these elements.

Suppose one atom of one element (let us call it A) unites with one atom of another element (B), and so on throughout the whole mass of the two elements ; it is evident that if there is the *same number* of atoms of each kind, none of either kind will remain uncombined when the action is complete.

Let us suppose, further, that the atoms of B are *twice* as heavy as the atoms of A. Then, if the elements unite atom for atom, the resulting compound will necessarily contain the elements in the proportion of *one* part, by weight, of A to *two* parts, by weight, of B. Or, if we analyze the compound consisting of A and B united atom for atom, and find that it contains *one* part, by weight, of A to *two* parts of B, we must conclude that the atom of B is twice as heavy as the atom of A.

In the light of the atomic theory, therefore, chemical action *must* take place between *definite masses* of substances. The theory is thus an explanation of the law of definite proportions (*cf.* § 69).

240. Explanation of the Law of Multiple Proportions. — The atomic theory is the explanation not only of the law of definite proportions, but also of that of multiple proportions. For, if atoms are indivisible, as their name indicates, elements that combine with one another in more than one proportion must do so in some way that will not require the dividing of an atom; that is to say, the elements A and B must unite in the proportion of *one* atom of A to *one* of B, or *one* of A to *two* of B, or *one* of A to *three* of B, or *two* of A to *three* of B, etc.

Let us suppose, as in § 239, that the atom of B is twice as heavy as that of A; then, if A and B combine atom for atom, it is evident that the compound formed will contain the elements in the proportion of *one* part, by weight, of A to *two* parts of B; but if *one* atom of A unites with *two* atoms of B, the resulting compound will contain the elements in the proportion of *one* part, by weight, of A to *four* parts of B.

Thus, if we assume the atomic hypothesis, it follows that elements which combine with one another in more than one proportion *must* do so according to the *law of multiple proportions.*

241. Distinction between Atoms and Molecules.— As has already been stated (*cf.* § 131), the *physical* properties of gases receive a reasonable explanation from the assumption that matter is composed of *molecules.* Molecules and atoms are *not identical;* for while atoms are thought of as the very smallest particles into which matter is *capable* of being divided, molecules are held to be the *aggregations of atoms* which form the *physical* units of matter. The atoms composing a molecule do not (usually) part company when matter undergoes a *physical* change.

To illustrate: The physical properties of ammonia are determined by the properties of the ammonia *molecules;* it is only when we subject ammonia to a *chemical* change that we *divide* the molecule. Then it is that the properties of the nitrogen and hydrogen atoms come into play.

The molecules of *elements* consist of atoms of only *one* kind; while the molecules of *compound* substances contain atoms of *two or more* kinds.

242. The Molecular Masses of Gaseous Substances.

— According to Avogadro's Rule (*cf.* § 133), the number of molecules in equal volumes of all gaseous substances is *approximately* the same. This means that a liter of *chlorine*, for example, contains practically as many chlorine molecules as there are hydrogen molecules in a liter of hydrogen, or hydrochloric acid molecules in a liter of hydrochloric acid gas, *if only the temperature and pressure are the same* in all cases.

The hypothesis applies not only to true gases, but also to the vapors of many substances ordinarily liquid or solid. Thus, a liter of steam, or one of acetic acid vapor, is assumed to contain practically as many molecules as a liter of hydrogen under the same conditions.

From the relative masses of equal volumes, *i. e.*, the *densities*, of gaseous substances, we can get the relative masses of molecules; for, if a liter of chlorine is found to weigh 3.18 grams and a liter of nitrogen, under the same conditions, 1.25 grams, and if the number of molecules in a liter of each is the same, the relative masses of the chlorine and nitrogen molecules must be as 3.18 : 1.25.

Moreover, since the relative masses of equal volumes of hydrogen, hydrochloric acid gas, steam, and oxygen, under the same conditions, are as 0.0896 : 1.63 : 0.8064 : 1.43, respectively, these numbers must express the relative masses of the molecules of the substances named.

Chemists have adopted as a standard the molecular mass of **oxygen** and have called it **32**. The reason for this will appear later (*cf.* § 256).

The molecular mass of hydrogen is thus determined from the proportion, —

Wt. of 1 liter of oxygen : Wt. of 1 liter of hydrogen :: molecular mass of oxygen : molecular mass of hydrogen ; or,

$$1.43 : 0.0896 :: 32 : x.$$
$$\text{Whence } x = 2.005.$$

By similar processes the molecular masses of chlorine, nitrogen, hydrochloric acid, and steam may be determined to be approximately 71, 28, 36.5, and 18, respectively.

243. Vapor Density Methods. — It is evident from the preceding section that we can determine the approximate molecular mass of a *gaseous* substance or of a substance that can readily be vaporized. We need only get the weight of a given volume of the substance in the gaseous state and compare this weight with that of an equal volume of oxygen. Methods for determining this ratio are called "*vapor density*" methods.

Suppose we wish to get the approximate molecular mass of *chloroform*, a substance boiling at 61° C., at ordinary pressure. Several vapor density methods are available; one of them is as follows: —

Victor Meyer's Method. — In the method of Victor Meyer (Fig. 56), a weighed amount of the chloroform (or other substance whose vapor density is to be found) is dropped into the tube *A* and vaporized; the air which is expelled through the delivery tube and collected in the graduated tube is a measure of the volume of the chloroform vapor. We thus obtain the weight of a given number of cubic centimeters of chloroform vapor. By comparing this weight with the weight of an equal volume of oxygen, we can get the molecular mass of chloroform.

The tube *A* is raised to any required temperature by boiling some liquid in the jacket *B*; in the case of chloroform, water might be used.

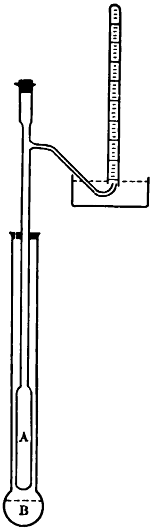


FIG. 56.

244. Other Methods of Determining Molecular Masses.

— Vapor density methods of determining molecular masses do not apply to substances that cannot be vaporized without decomposition nor to those whose boiling temperatures are so high as to be practically unattainable. For soluble substances, however, other methods can be used. These methods are based upon the fact that substances in dilute solution behave much as they would if they were gaseous (*cf.* §§ 138 and 139) and occupied the same volume as is occupied by the solution.

Thus, if we take two substances whose molecular masses have been determined in other ways and dissolve equal quantities of them in equal amounts of the same solvent, we shall find that the *osmotic pressures* of the two solutions are *proportional to the molecular masses of the dissolved substances.* That is to say, the *number* of the dissolved molecules, and not their *nature*, determines the osmotic pressure.

By comparing the osmotic pressure of a substance of *known* molecular mass with that of one whose molecular mass is *unknown*, the unknown molecular mass might be found.

The osmotic pressure method is not used much, because two other effects due to dissolved molecules are more readily measured; these are (1) the *raising of the boiling point of the solvent* and (2) *the depression of its freezing point.*

245. Boiling Point and Freezing Point Methods. — If we compare the temperature of boiling pure water with that of water containing a dissolved substance, *e. g.*, sugar, we shall find that the dissolved substance causes the water to boil at a higher temperature. This is true in general; a dissolved substance ***raises*** the boiling temperature of the solution above that of the pure solvent.

For *dilute* solutions, increasing the relative quantity of the dissolved substance increases the rise of the boiling temperature *proportionally*.

Moreover, if two substances of known molecular masses are dissolved in amounts proportional to their molecular masses in equal quantities of the same solvent, the rise of the boiling point is the *same* in the two cases. But, *taking substances in quantities proportional to their molecular masses is the same as taking equal numbers of molecules;* hence the rise of the boiling point, like the osmotic pressure, is proportional to the *number* of dissolved molecules.

The freezing point of a solution, on the other hand, is *lower* than that of the pure solvent; but the *amount* that the freezing point is depressed, like the rise in the boiling temperature, is proportional to the *number* of dissolved molecules, and *independent of their nature.* Therefore, if substances are dissolved in equal amounts of a given solvent *in quantities proportional to their molecular masses,* the freezing points of the solutions are lowered to the *same* degree.

There are thus both freezing point and boiling point methods for determining the molecular masses of many substances that cannot be handled by vapor density methods.

246. Methods of Obtaining Exact Molecular Masses. — All of the methods described give only *approximate* molecular masses; *exact* molecular masses are found by quantitative analysis.

Thus, the per cent of chlorine in hydrochloric acid is 97.26. This number, must, therefore, be to 100, the total per cent, as the mass of chlorine in the molecule is to the mass of the *whole* molecule, or.

$$97.26 : 100 :: x : 36.5.$$

Whence $x = 35.5$, *approximately.*

In the same way the mass of all the chlorine atoms contained in the molecule of each of the other compounds can be found.

It will be observed that the *greatest common factor* of all the numbers representing the masses of chlorine in the molecules of the compounds given in the list is 35.5; a study of the other compounds of chlorine only *confirms* the choice of this number. *Thirty-five and five-tenths* is, therefore, taken as the approximate atomic mass of chlorine.

The general method of selecting the atomic masses of such elements as hydrogen, nitrogen, bromine, iodine, carbon, sulphur, phosphorus, arsenic, and some others is as given for chlorine. We get the molecular mass and the percentage composition of each of the known compounds of the element; the *greatest common factor* of the numbers representing the masses of the element found in the molecules of all its compounds will be the atomic mass of the element.

Note that the atomic mass found in this way is the *greatest* atomic mass the element can have. The study of other compounds of the element *may* make it necessary for chemists to choose some *sub-multiple* of the maximum atomic mass, but never a multiple of it.

249. Exact Atomic Masses. — If the molecular masses of the compounds from a consideration of which the atomic mass of an element is chosen have been determined *accurately*, i. e., by quantitative methods, the atomic mass of the element will be accurate; but if the molecular masses of the compounds were determined by vapor density methods, as in the case of the chlorine compounds in § 248, the atomic mass will be only *approximate.*

Exact atomic masses are determined by comparison with oxygen, whose atomic mass is chosen 16. Formerly hydrogen was used as the standard, its atomic mass being chosen 1. But oxygen forms compounds with so many more elements than hydrogen does, that atomic masses can be determined more directly, and hence more *accurately*, if oxygen is taken as 16.

The list of atomic masses is given in the *Appendix.*

250. Dulong and Petit's Rule. — A rapid method of getting at the approximate atomic masses of *solid* elements, especially *metals*, is based upon the relation between the *specific heat* (better, *relative thermal capacity*) of an element and its atomic mass.

By the **specific heat** *of a substance we mean the quantity of heat required to raise the temperature of a certain mass of the substance one degree of temperature as compared with the amount needed to raise the temperature of an equal mass of water one degree.* To illustrate: if two iron balls of equal mass and at the same temperature, say at 200° C., are put into equal and sufficiently large masses of water and mercury, it is evident that the same *quantity* of heat will be imparted in the two cases. The temperature effect will, however, be very different; for the mercury will be heated through about 32 times as many degrees as the water.

Thus the specific heat of mercury is $\frac{1}{32}$, or 0.0319.

In 1819, Dulong and Petit observed the existence of the rule which is called by their names; the rule may be stated as follows: —

The specific heat of a solid element multiplied by its atomic mass is a constant (about 6.25). Some illustrations appear in the following table: —

ELEMENT.	SPECIFIC HEAT.		ATOMIC MASS.		ATOMIC HEAT.
Sodium.	0.29	×	23	=	6.7
Potassium.	0.166	×	39	=	6.5
Iron.	0.112	×	56	=	6.3
Silver.	0.057	×	108	=	6.1
Tin.	0.054	×	118	=	6.4
Gold.	0.032	×	196	=	6.3
Mercury (solid).	0.032	×	200	=	6.4
Lead.	0.031	×	206.4	=	6.4

The table shows that the higher the atomic mass is, the lower is the specific heat. The complete list of specific heats is given in the *Appendix.*

It is apparent that the rule of Dulong and Petit may be used to determine the *approximate* atomic mass of an element. Thus, knowing the specific heat of ***cadmium*** to be 0.0567, we can at once get its approximate atomic mass. We simply solve for x in the equation,

$$\frac{6.25}{0.0567} = x.$$

Hence $x = 110$.

The exact atomic mass of cadmium is about 112.

251. Application of Atomic Mass Methods. — The methods used in actually getting the atomic mass of an element may be illustrated by the the case of *zinc*. The method used for chlorine will not apply here; we must, therefore, study the action of zinc with elements of *known* atomic mass, *e. g.*, with hydrogen, chlorine, and oxygen.

When zinc is dissolved in certain dilute acids, it sets free hydrogen; we can thus get the relation between the mass of zinc taken and that of the hydrogen displaced, *i. e.*, the equivalent of the zinc. Now, if for each atom of zinc dissolved an atom of hydrogen is set free, the mass of the zinc must be to the mass of the hydrogen as the atomic mass of zinc is to the atomic mass of hydrogen. Since we know the atomic mass of the hydrogen, we could calculate that of the zinc.

The relation of zinc to hydrogen is about as 32.7 : 1.

A second element with which we can compare zinc is chlorine. The compound of these two elements, zinc chloride, may be made either (1) by dissolving zinc in hydrochloric acid and evaporating the solution, or (2) by burning zinc in chlorine.

The relation of zinc to chlorine in zinc chloride, as determined by quantitative analysis, is about as 32.7 : 35.5. Hence, if chlorine and zinc have united atom for atom, and the atomic mass of chlorine is 35.5, the atomic mass of zinc must be 32.7.

Let us, however, consider a *third* compound of zinc, viz., its *oxide.*

This substance may be made by heating zinc in oxygen, or, better, by dissolving zinc in dilute nitric acid and heating the zinc nitrate formed to a high temperature.

The proportions of the elements in zinc oxide are, — zinc, 65.4 parts, to oxygen, 16 parts.

Here, also, we might assume that zinc and the other ~~element~~ are united atom for atom; if so, the atomic mass of zinc is *65.4*.

To compare these results let us write them down together : —

(1) One part of hydrogen (1 atom) was replaced by 32.7 parts of zinc.

(2) Thirty-five and five-tenths parts of chlorine (1 atom) united with 32.7 parts of zinc.

(3) Sixteen parts of oxygen (1 atom) united with 65.4 parts of zinc.

Evidently we cannot assume that one atom of zinc unites with one atom of the other element in each of the three cases; for we cannot have some zinc atoms with a mass of 32.7 each, and others with a mass twice as great.

If the atomic mass of zinc is 32.7, *one* atom of oxygen must unite with *two* atoms of zinc to form zinc oxide; if, however, the atomic mass of zinc is 65.4, *two* atoms of hydrogen must have been replaced by *one* of zinc, and *two* atoms of chlorine must have united with *one* of zinc.

The *molecular mass* of zinc chloride, or of zinc oxide, would help us; that of zinc chloride is the one used; for the weight of a known volume of its vapor has been obtained. By a solution of the proportion,

Wt. of 1 liter of zinc chloride vapor : wt. of 1 liter of oxygen (under the same conditions) :: molecular mass of zinc chloride : molecular mass of oxygen, *i. e.*, 32 (*cf.* § 242),

the molecular mass of zinc chloride was found in an actual experiment to be about 134. This result is sufficiently accurate to enable us to decide that the molecular mass of zinc chloride is 136.4 rather than *one-half* or *twice* this number.

A molecule of zinc chloride thus contains 65.4 parts of zinc and 71 parts (two atoms) of chlorine. We do not, however, know whether the two atoms of chlorine are united with *one* atom of zinc having a mass of 65.4, or with *two*, each having a mass of 32.7; or with *three*, each having a mass of 21.8, etc.

We now apply Dulong and Petit's rule. By substituting the specific heat of zinc, found by experiment (0.094), in the expression,

$$\frac{6.25}{\text{specific heat}} = \text{atomic mass},$$

we obtain 66.5 for the *approximate* atomic mass of zinc. This shows us that the number 65.4 is to be taken rather than any sub-multiple of it.

252. How Formulas are Determined. — If we know the *molecular mass* of a compound, the *parts per cent* of each element in the compound, and the *atomic masses* of the elements, we can determine the formula of the compound.

To illustrate: A certain compound of carbon and hydrogen is found by vapor density methods to have the molecular mass 72. The per cent of carbon is 83.33 and that of the hydrogen 16.67. The mass of all the carbon atoms in the molecule must be 60 ($= 72 \times .8333$), and the mass of all the hydrogen atoms 12. Since the mass of each carbon atom is 12, there must be 5 atoms of carbon in the molecule of the compound; and since the mass of each hydrogen atom is 1, there must be 12 hydrogen atoms. Hence the formula is C_5H_{12}.

If the molecular mass is not known, we cannot be sure whether we have the correct formula or not. Thus the formulas $C_{10}H_{24}$, $C_{20}H_{48}$, etc., would all have the same quantitative composition as C_5H_{12}. This may be illustrated by the following case: —

The substances *formaldehyde*, *acetic acid*, and *grape-sugar* all have the same quantitative composition, viz.: —

Carbon, 40.00%;
Hydrogen, 6.67%;
Oxygen, 53.33%.

What are their formulas?

We can get the relation between the *numbers* of atoms of each element in the molecule by dividing the per cent of each element by the atomic mass. This gives, —

C, 3.33 (= 40 ÷ 12);
H, 6.67 (= 6.67 ÷ 1);
O, 3.33 (= 53.33 ÷ 16).

Since there cannot be 3.33 or 6.67 atoms, we find the simplest relation between these numbers.

$$3.33 : 6.67 : 3.33 :: 1 : 2 : 1.$$

Hence, the simplest formula a substance of the given composition could have is CH_2O. Such a substance would have a molecular mass of 30. This is the molecular mass of *formaldehyde;* hence, the formula of formaldehyde is CH_2O. The molecular mass of acetic acid is 60, and that of grape-sugar, 180; hence the formulas of these substances are $C_2H_4O_2$ and $C_6H_{12}O_6$ respectively.

253. Molecular Formulas and Equations. — The symbol of an element means not only the element *in general* (*cf.* § 5) and a definite *mass* of it, but also an *atom* of it. As symbols stand for *atoms*, so formulas represent *molecules.* The numbers which we called *combining proportions* in § 75 and § 76, because they represent the proportions *by weight* in which elements and compounds enter into reactions, were derived from the commonly accepted atomic and molecular masses. The equations previously given may thus be looked upon as representing changes in the arrangement of the atoms composing molecules.

The equation for the action of zinc and sulphuric acid, for example, means that one *atom* of zinc reacts with one *molecule* of sulphuric acid to form a *molecule* of zinc sulphate and two *atoms* of hydrogen. The hydrogen we obtain by this reaction is not, however, hydrogen in the form of *atoms*, but of *molecules;* for the atoms have *united* with one another, every two forming a *molecule* of hydrogen. Hence we write H_2, meaning *one molecule* of hydrogen (consisting of two atoms), rather than 2 H, which means simply *two atoms* of hydrogen. For the same reason we write the equation for the union of hydrogen and oxygen, $2H_2 + O_2 = 2H_2O$; and not $4H + 2O = 2H_2O$; nor yet $2H + O = H_2O$.

254. Nascent, or Atomic, State. — In general, we represent the factors and the products of equations by *molecular formulas* instead of by *atomic symbols.* We do this because we believe that elements in the *free* condition usually consist *not* of atoms but of *molecules* made up of two or more atoms united.

Thus, although oxygen, hydrogen, chlorine, etc., are set free from the molecules of their compounds in the form of *atoms*, they do not remain so; for the atoms unite to form molecules. In fact, an element like oxygen is in the atomic condition only during the infinitely short time that intervenes between the liberation of the atoms from molecules and their union with other atoms to form *new* molecules.

A proof of this is the fact that an element has properties at the *instant* of its liberation from a compound, *i. e.*, in its **nascent** condition, which differ from those we ordinarily recognize as belonging to the element. Thus, when chlorine liberates oxygen from water (*cf.* § 88) in the process of bleaching, the *nascent* oxygen is much more active than ordinary oxygen. Many other cases of the same kind are known.

The nascent state and the atomic state of an element thus coincide.

255. Number of Atoms in the Molecules of Elements. — We have just learned that the molecules of hydrogen and oxygen consist of two atoms each; the same fact is true of several other elementary gases.

We can reason that the molecules of oxygen must consist of *at least* two atoms each from the proportions by volume in which hydrogen and oxygen combine. We can represent these proportions *graphically* by letting squares represent *equal volumes* of the gases hydrogen and oxygen, and of the steam formed by their union.

□□ + □ = □□
2 vols. hydrogen 1 vol. oxygen 2 vols. steam.

Now, according to Avogadro's rule, the number of molecules of hydrogen and oxygen in equal volumes must be approximately equal; hence, —

Two *molecules* of hydrogen + 1 *molecule* of oxygen give 2 *molecules* of steam.

To form *one* molecule of steam, however, we must imagine union to take place between *one* molecule of hydrogen and *one-half* a molecule of oxygen. This *half-molecule* of oxygen is the *atom* of oxygen.

That the molecules of hydrogen and of chlorine contain *two atoms* is evident from a similar method of reasoning; for, since one volume of hydrogen and one volume of chlorine give *two* volumes of hydrochloric acid (*cf.* § 94), one *molecule* of hydrogen and one *molecule* of chlorine must give *two* molecules of hydrochloric acid. Therefore, one molecule of hydrochloric acid must contain *one-half a molecule* of hydrogen and *one-half a molecule* of chlorine. Here again the half-molecules are the *atoms* of these gases.

Methods are known for determining the number of atoms in the molecule of an element in the gaseous state; the results obtained agree with those deduced by our reasoning. No reactions now known make it necessary for us to assume that there are *more* than two atoms in the molecules of hydrogen, oxygen, nitrogen, chlorine, and fluorine. Some other elements, not *ordinarily* gaseous, have two atoms to the molecule *in the gaseous state.* In other cases the molecule consists of only *one* atom; in others still, of three or more atoms.

256. Reason for Choosing 32 as the Molecular Mass of Oxygen. — We can see now why the molecular mass of oxygen was taken as 32 (*cf.* § 242). For, if the mass of the oxygen *atom*, i. e., the *half-molecule*, is assumed to be exactly 16 (*cf.* § 249), the mass of the molecule must be twice as great. Formerly, when the mass of the hydrogen *atom* was taken as the standard for *atomic* masses, the mass of the hydrogen *molecule* (= 2) was taken as the standard for *molecular* masses.

257. Laws of Simple and Multiple Volumes. — *Gaseous* bodies combine in definite proportions not only by *weight*, as do liquids and solids as well, but also by *volume*. This was the case when oxygen and hydrogen united to form steam (*cf.* § 38), and when hydrogen and chlorine gave hydrochloric acid gas (*cf.* § 94). The relation between the volumes of the combining gases and the volumes of the products, if these are gaseous, is also *simple* and *definite*. Thus, two volumes of hydrogen and one of oxygen give, on union, *two* volumes of steam; and three volumes of hydrogen and one of nitrogen give *two* of ammonia.

These and other facts give a basis for the **Law of Simple Volumes,** which is: *The volumes of reacting gaseous substances have a simple relation with one another and with the volumes of the products, if these are gaseous.*

Just as we have a *Law of Multiple Proportions by Weight*, so we have a **Law of Multiple Volumes.** It is stated thus: *If two gases unite in more than one proportion, and we consider the volume of one as fixed, then the several volumes of the second gas that unite with the fixed volume of the first are in a simple relation to one another.*

Thus, the volumes of nitrogen which unite with one volume of oxygen to form nitrous oxide (N_2O) and nitric oxide (NO) are as 2 : 1 respectively (*cf.* §§ 170 and 171).

258. Volumetric Meaning of an Equation. — Since the formula of a gaseous substance means a *molecule* of the substance, it means also a *volume* of it; for equal volumes contain approximately equal numbers of molecules.

Thus, in the equation,

$$2\,H_2 + O_2 = 2\,H_2O,$$

H_2 means *one volume* of hydrogen; and 2 H_2, *two* volumes. O_2 means *one volume* of oxygen; 2 H_2O means *two* volumes of steam.

So the equation $N_2 + 3\,H_2 = 2\,NH_3$ means that *one volume* of nitrogen and *three* volumes of hydrogen unite to give *two* volumes of ammonia. These relations have all been proved by experiment.

From a correctly written equation we can, therefore, know in what proportions *by volume* gaseous substances unite.

Thus, the equation,

$$2\,CO + O_2 = 2\,CO_2,$$

shows that one volume of oxygen unites with *two* of carbon monoxide, forming *two* of carbon dioxide. In other words, the *volume* of the carbon dioxide formed by burning a given volume of carbon monoxide is just equal to the volume of the carbon monoxide.

The equation,

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O,$$

(*cf.* § 218) shows that *one* volume of marsh gas uses up *two* volumes of oxygen in forming *one* volume of carbon dioxide and *two* volumes of steam.

If a substance that appears in a reaction is not known in the gaseous state, nothing can be said of its volume.

Thus, the equation, $C + O_2 \longrightarrow CO_2$, tells us that one volume of oxygen disappears in the formation of one volume of carbon dioxide; but it does not tell us the volume of the carbon that unites with one volume of oxygen, since we cannot experiment with *gaseous* carbon.

259. Valence. — The student must have noticed from the formulas previously studied that atoms differ greatly in their power of combining with other atoms. Thus, the formulas of the compounds of *hydrogen* show interesting differences; for, while in the case of hydrochloric acid *one* atom of chlorine unites with *one* of hydrogen, in the case of water (H_2O) one atom of oxygen holds *two* of hydrogen. The combining powers of the nitrogen and the carbon atom are still greater; for in the molecule of ammonia (NH_3) one nitrogen atom holds *three* hydrogen atoms; and in the molecule of marsh gas (CH_4) one carbon atom holds *four* atoms of hydrogen.

This power of the atoms to unite with different numbers of other atoms is called valence. An element like chlorine, whose atom can hold only *one* atom of hydrogen, is said to have a *valence of* **one**, or to be **univa-**

lent. The hydrogen atom is always considered univalent.

An element like oxygen, whose atom can hold *two* hydrogen atoms, is said to have a *valence of* **two,** or to be **bivalent.** One like nitrogen is, therefore, **trivalent;** and one like carbon, **quadrivalent.**

Valence is not only the power of *combining with,* but also of *replacing,* different numbers of atoms. Thus, the formula of *potassium sulphate,* $\begin{matrix}K\\K\end{matrix}SO_4$, is derived from that of *sulphuric acid,* $\begin{matrix}H\\H\end{matrix}SO_4$, by replacing two hydrogen atoms by two of potassium. Potassium has, therefore, a valence of *one.*

In the case of *zinc nitrate,* $Zn\begin{matrix}NO_3,\\NO_3,\end{matrix}$ *one* atom of zinc has replaced *two* hydrogen atoms (in 2 HNO_3) ; hence zinc is *bivalent.* Similarly, *iron* is *trivalent* in *ferric phosphate,* $FePO_4$; for the formula of phosphoric acid is H_3PO_4. *Aluminum,* also, is trivalent in *aluminum sulphate,* $Al_2\,(SO_4)_3$; for *two* aluminum atoms, each with a valence of *three,* replace *six* hydrogen atoms (in 3 H_2SO_4).

The valence of an element is often represented by small *Roman* figures placed a little *above* and to the *right* of the symbol of the element. Thus, Al^{III} means *trivalent* aluminum; Hg^{I}, *univalent* mercury; and Pt^{IV}, *quadrivalent* platinum.

260. Different Formula Types Based on Valence. — A *bivalent* element, like oxygen, unites with *two* atoms of a *univalent* element, but with only *one* of another bivalent element. Thus, *calcium chloride* has the formula $CaCl_2$; but *calcium oxide* has the formula CaO.

When a *bivalent* element unites with a *trivalent* element, *two* atoms of the trivalent element generally require *three* of the bivalent one. This is shown in the formulas Al_2O_3 for aluminum oxide, As_2S_3 for arsenious sulphide, and Mg_3N_2 for magnesium nitride.

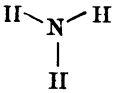
When *quadrivalent* atoms, like those of carbon and silicon, unite with univalent atoms, *four* of the univalent atoms are required, as in CH_4 and $SiCl_4$; when they unite with bivalent atoms, *two* of the latter are usually required, as in CS_2 and SiO_2.

The valence of an element is not, however, *fixed;* for carbon forms the compound CO, in which its valence is undoubtedly *two*. So, also, nitrogen is *trivalent* in the compounds NH_3 and N_2O_3, but *quinquivalent* in NH_4Cl and N_2O_5.

261. Graphic Formulas. — By means of the idea of valence, we may represent the relation of atoms to one another in molecules. When the molecule consists of *two* atoms, only one arrangement is possible, viz., the atoms are joined directly. Thus in *hydrochloric acid* and in *molecular* hydrogen we have simple union. If we represent the combining power of the elements by lines (called *bonds*), we may write the formula for hydrochloric acid *graphically* $H—Cl$ and that of hydrogen $H—H$. The single line shows that the valence of each atom in the molecule is *one*.

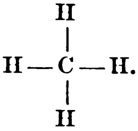
Everything goes to show that the two hydrogen atoms in the water molecule are not united to each other, but to oxygen. Similarly it is believed that the hydrogen atoms of the ammonia molecule are all united to nitrogen, and those of the marsh-gas molecule to carbon. We may represent these facts in the formulas, —

$H—O—H$;



$$\begin{array}{ccc} H & & H \\ & N & \\ & | & \\ & H & \end{array}$$

; and

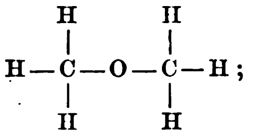


$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & H. \\ & & | & & \\ & & H & & \end{array}$$

Formulas like those just given are called *graphic* or *structural* formulas. We may represent an element in its nascent state by the symbol with *free* valence bonds. Thus, — O — represents *nascent* or atomic oxygen; H —, nascent hydrogen.

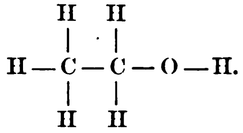
262. Isomerism. — Many cases are known in which two or more compounds have the same composition and molecular mass but different properties. Methyl ether and ethyl alcohol, for example, are both represented by the formula C_2H_6O; these substances are so different, however, that no one would mistake one for the other. Thus, methyl ether boils at —24° C., at ordinary pressure, while ethyl alcohol boils at +78° C. Such compounds are said to be **isomeric** with each other.

By the use of graphic formulas, the difference in character between these isomeric substances is readily represented. Thus, the graphic formula for methyl ether is, —



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H; \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

while that of alcohol is, —



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H. \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

According to these formulas, all the hydrogen atoms of methyl ether have the *same relation* to the remainder of the molecule and should behave in the same way with reagents; while in the case of ethyl alcohol *one* hydrogen atom — the one bound to oxygen — should be *different* from the other five. This is actually the case;—for the atom of hydrogen bound to oxygen is the only one of the six that can be replaced by sodium and other metals.

263. **Allotropism.** — Just as there are compounds having the *same chemical composition* which are yet very *unlike* in their properties, so there are elements existing in forms so different that they might easily be supposed to be entirely different substances. In the preceding section we have called the compounds *isomers;* the different forms of the same element are called **allotropic forms** of the element. The existence of an element in different forms is called **allotropism.** Carbon and sulphur, as we have already learned, exist in several allotropic forms; the same is true of oxygen, phosphorus, silicon, boron, etc.

Allotropism is probably due to different causes, such as different *arrangements* of the atoms in the molecule, or different *numbers* of atoms in the molecule.

In many cases an allotropic form is only *temporary*. This is true of the plastic, or amorphous, modification of sulphur (*cf.* § 175), which changes into the ordinary form with *evolution of heat*. Plastic sulphur thus represents a condition of *unstable equilibrium*, like a compound which has a *negative* heat of formation (*cf.* § 235).

264. Exercises.

1. (*a*) A liter of a certain gaseous substance weighs approximately 1.966 grams at standard conditions; what is its molecular mass? (See § 242.)

(*b*) If $\frac{3}{11}$ of this substance is carbon and $\frac{8}{11}$ oxygen, what is its formula? (See § 252.)

2. (*a*) Two hundred c.c. of a gas weigh 0.3932 grams at standard conditions; what is the molecular mass?

(*b*) Analysis shows that the gas is composed of nitrogen, 63.64%, and oxygen, 36.36%; what is the formula?

3. The oxide of magnesium is composed of magnesium, 60%, oxygen, 40%; what is its simplest formula?

4. A chloride of phosphorus has the composition, phosphorus 22.55%, chlorine 77.45%; find its simplest formula.

5. What is the approximate atomic mass of platinum if its specific heat is about 0.033?

6. What volume of oxygen is used up when 20 c.c. of acetylene burn in air? What is the volume of carbon dioxide formed? (*Cf.* §§ 221 and 258.)

7. Write the *molecular* equation for the combustion of *pentane*, C_5H_{12}, in oxygen, if the products are carbon dioxide and water.

What volume of oxygen is used up when 50 c.c. of pentane burn?

What volume of carbon dioxide is produced?

8. Knowing that the valence of an element x is *1*, write the simplest formula for its *sulphate*, its *carbonate*, and its *nitrate*.

9. Write the simplest formulas of the *chloride* and *sulphite* of an element whose valence symbol is Sr^{II}.

CHAPTER XVII.

FLUORINE, BROMINE, IODINE, AND THEIR COMPOUNDS.

265. Halogens. — The elements *fluorine*, *chlorine*, *bromine*, and *iodine* are called "the halogens," from *hals*, Greek for "salt," and the suffix *gen*, meaning "a constituent of," as in "hydrogen," etc.

Fluorine and chlorine are gaseous at the ordinary temperature ; bromine is a liquid boiling at about 59° C. ; while iodine is a black solid which gives off, even at ordinary temperatures, a beautiful violet vapor.

266. Fluorine. — The element fluorine was known in its compounds long before it was obtained in the *free* condition. The most common of its compounds is *calcium fluoride*, or fluorspar, $CaFl_2$. Fluorspar derives its name from *fluo*, Latin for "to flow," and *spar*, meaning "a rock." The name is applied to this substance owing to the use of fluorspar as a *flux* in metallurgy.

A flux is an easily fusible substance added to the mixture of an ore and a reducing agent to promote *fusion* of the mixture. The substance resulting from the union of the flux with the impurities present is usually called "slag."

Another important natural fluorine compound is *cryolite*. This is a *double* fluoride of *aluminum* and *sodium* : its formula is $AlFl_3 . 3\, NaFl$ or Na_3AlFl_6.

Fluorine cannot be prepared from either of these compounds *directly*, but has been made (1886) by the electrolysis of *anhydrous* hydrofluoric acid, HFl.

$$2\ HFl = H_2 + Fl_2.$$

The operation may be carried out in copper or platinum apparatus, but not in glass, since hydrofluoric acid attacks glass energetically.

267. Properties of Fluorine. — Fluorine is a yellow gas, about one and two-fifths times as heavy as air. It acts upon water with violence, according to the equation,

$$2\ H_2O + 2\ Fl_2 \longrightarrow 4\ HFl + O_2.$$

The oxygen formed always contains some *ozone* (*cf.* § 287).

Fluorine unites with hydrogen explosively, *even in the dark* (*cf.* Chlorine, § 84), to form hydrofluoric acid. It forms no compounds with oxygen, so far as known. As commonly prepared, fluorine acts upon *glass*, but this is due to the fact that a small amount of hydrofluoric acid is present in the fluorine.

Fluorine acts readily upon silicon and antimony, forming the corresponding *fluorides*, $SiFl_4$ and $SbFl_3$.

Gaseous fluorine has been condensed to a liquid boiling at —187° C. at ordinary pressure.

268. Hydrofluoric Acid. — Hydrofluoric acid is commonly prepared by heating calcium fluoride with concentrated sulphuric acid. The equation is, —

$$CaFl_2 + H_2SO_4 = CaSO_4 + 2\ HFl.$$

Bromine may also be prepared by conducting the proper amount of *chlorine* into the solution of a bromide. With magnesium bromide the equation is, —

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2.$$

270. Properties of Bromine. — Bromine is a brown liquid about 3.2 times as heavy as water. Its vapor has an odor much like that of chlorine, and affects the eyes. Bromine boils at about 59° C.

The density of bromine vapor shows that the molecule is *diatomic;* its formula is, therefore, Br_2. At about 1000° C. the molecule begins to dissociate into molecules containing only *one* atom each (*cf.* § 45).

Bromine dissolves in water, carbon disulphide, and other solvents. The aqueous solution is called "bromine water."

In the presence of some substance capable of taking up oxygen, bromine reacts with water energetically, according to the equation,

$$H_2O + Br_2 \longrightarrow 2\ HBr + (-O-).$$

By —O— we mean *nascent* oxygen (*cf.* § 261). Bromine water is thus a good *oxidizing* agent.

The same action goes on more slowly when no oxidizable substance is present; bromine water thus becomes converted into a dilute solution of hydrobromic acid, HBr.

Bromine is less active than chlorine, but, like chlorine, it unites with hydrogen and with metals to form bromides.

271. Hydrobromic Acid. — Hydrobromic acid cannot be made in a pure state by treating a bromide with concentrated sulphuric acid, for the reason that some of the hydrobromic acid formed breaks up into hydrogen and bromine, and the *nascent* hydrogen *reduces* the sulphuric acid. The products of the action are thus *bromine* and *sulphurous acid*, as well as hydrobromic acid. These facts are represented in the equations,

$$(1)\ NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr;$$
$$(2)\ 2\,HBr + H_2SO_4 \longrightarrow H_2O + Br_2 + H_2SO_3.$$

The method commonly used to prepare hydrobromic acid is to treat red phosphorus with bromine in the presence of water. The phosphorus and bromine first unite to form phosphorus tribromide, PBr_3; but this substance is decomposed at once by the water to form phosphorous acid and hydrobromic acid. The equations are, —

$$(1)\ 2\,P + 3\,Br_2 = 2\,PBr_3;$$
$$(2)\ PBr_3 + 3\,H_2O = H_3PO_3 + 3\,HBr.$$

The phosphorous acid, being non-volatile, remains behind; while the gaseous hydrobromic acid passes off. The hydrobromic acid may be freed from bromine vapor by passing it through a U-tube containing *moist* red phosphorus.

272. Properties of Hydrobromic Acid. — Hydrobromic acid gas is like hydrochloric acid gas. It *fumes* in the air and dissolves readily in water. Its concen-

Phosphorus tri-iodide is first formed, but is decomposed at once according to the equation,

$$PI_3 + 3\ H_2O = H_3PO_3 + 3\ HI\ (cf.\ \S\ 271).$$

An aqueous solution of hydriodic acid may best be prepared by making use of a property common to chlorine, bromine, and iodine, viz., the ability of each of these substances to decompose *hydrogen sulphide*. The sulphur formed, being insoluble, is precipitated; hence the reaction goes on to completion (*cf.* § 180). The equation in the case of iodine is,

$$2\ I + H_2S \longrightarrow 2\ HI + S.$$

The hydrogen sulphide is conducted into a mixture of iodine and water until the iodine disappears. The sulphur is then filtered off, and the filtrate distilled. After the water has passed off, a heavy liquid is obtained, which boils at 126° C. This is about 57% hydriodic acid.

276. Properties of Hydriodic Acid. — Hydriodic acid gas is about 4.4 times as heavy as air. Like hydrochloric and hydrobromic acids, it is very soluble in water. One cubic centimeter of water at 10° C. and standard pressure dissolves about 450 c.c. of the gas.

Hydrogen and iodine can be made to unite under appropriate conditions. When uniting they do not *evolve* heat, but *absorb* it. This accounts for the fact that hydriodic acid is so unstable (*cf.* § 235).

The dissociation of hydriodic acid is like that of steam (*cf.* § 45). At any temperature above the point at which dissociation begins, the *decomposition* of hydriodic acid into hydrogen and iodine goes on side by side with *recombination* of hydrogen and iodine to form hydriodic acid. The condition of equilibrium is reached when as many molecules of hydriodic acid are *formed* in a given time as are *decomposed* in the same time. We may represent this condition of equilibrium by the equation,

$$2\ HI \rightleftarrows H_2 + I_2.$$

Such an equation is called a "balanced" or "equilibrium" equation. The arrows indicate that the reaction goes in both directions.

If either product of dissociation is removed from the "sphere of action," the dissociation goes on to completion. Thus, if silver is placed in hydriodic acid solution, it unites with the iodine as rapidly as iodine is formed. Hence hydrogen is set free.

$$2\ Ag + 2\ HI \longrightarrow 2\ AgI + H_2.$$

Because of its ready dissociation, hydriodic acid acts as a powerful *reducing* agent. Oxygen, or any oxidizing agent, gives with it *iodine* and *water*.

$$4\ HI + O_2 \longrightarrow 2\ H_2O + 4\ I.$$

277. Compounds of the Halogens with Oxygen. — Only three halogen oxides have been actually made; although more — especially one oxide of bromine — are suspected to be capable of existing. The three oxides definitely known are: —

Chlorine monoxide, Cl_2O;
Chlorine dioxide, ClO_2 or Cl_2O_4;
Iodine pentoxide, I_2O_5.

Chlorine monoxide is an unstable liquid which boils at +5° C. It explodes with violence. When *one volume* of chlorine monoxide is carefully decomposed, it gives *half a volume* of oxygen and *one* volume of chlorine.

Chlorine dioxide (ClO_2) and *tetroxide* (Cl_2O_4) correspond to the nitrogen oxides NO_2 and N_2O_4. It is formed with violent explosion when concentrated sulphuric acid acts upon potassium chlorate. The preparation of this substance should not be attempted without *precise directions* and *extraordinary precautions.*

Chlorine dioxide is a reddish-brown liquid, boiling at about 10° C.

Iodine pentoxide is the only oxide of iodine known at present. It is a white, stable powder; with water it gives iodic acid,

$$I_2O_5 + H_2O = 2\,HIO_3.$$

Iodine pentoxide is thus the *anhydride* of iodic acid.

278. Compounds of the Halogens with Oxygen and Hydrogen. — Compounds of the halogens with oxygen and hydrogen are called *oxygen acids*, or oxy-acids, of the halogens. They are more numerous than compounds with oxygen alone; for they include at least *three* chlorine acids, *three* bromine acids, and *two* iodine acids. The formulas of these acids appear in the following table: —

$HClO$.	$HBrO$.	
$HClO_2$ $\left\{\begin{matrix}\text{known only}\\ \text{in its salts}\end{matrix}\right\}$.		
$HClO_3$.	$HBrO_3$.	HIO_3.
$HClO_4$.	$HBrO_4$.	HIO_4.

279. Hypochlorous Acid, H–O–Cl. — Hypochlorous acid is present in a solution of chlorine in water (*cf.* § 85).

The equation for the action of chlorine upon water is a "balanced" one, viz.,

$$H_2O + Cl_2 \rightleftarrows HOCl + HCl;$$

there is, therefore, an *equilibrium* between these four substances. If a substance is present which is capable of taking up oxygen, the products of the action are hydrochloric acid and *nascent* oxygen, —

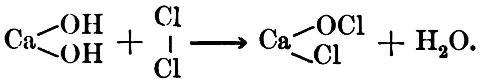
$$HOCl + HCl \longrightarrow 2\,HCl + (-O-).$$

In the presence of *sunlight* a concentrated solution of chlorine in water gives off oxygen (*cf.* § 85).

Salts of hypochlorous acid, i. e., *hypochlorites*, are formed by passing chlorine into *dilute* solutions of hydroxides of the metals. The amount of chlorine used must be less than is required to saturate the hydroxide. With potassium hydroxide the equation is, —

$$2\,KOH + Cl_2 \longrightarrow KOCl + KCl + H_2O.$$

When chlorine acts upon powdered slaked lime, $Ca(OH)_2$, *bleaching powder* $\left(Ca\begin{matrix}\nearrow OCl\\ \searrow Cl\end{matrix}\right)$ is produced.



$$Ca\begin{matrix}\nearrow OH\\ \searrow OH\end{matrix} + \begin{matrix}Cl\\ |\\ Cl\end{matrix} \longrightarrow Ca\begin{matrix}\nearrow OCl\\ \searrow Cl\end{matrix} + H_2O.$$

280. Chlorous Acid, H–O–Cl=O. — Chlorous acid does not exist free. Its potassium salt is produced, in solution, when an aqueous solution of chlorine dioxide, ClO_2, is treated with potassium hydroxide.

281. Chloric Acid, $H{-}O{-}Cl\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$. — Chloric acid is known only in its aqueous solution; this may be concentrated until it contains 40% of chloric acid. Chloric acid is a powerful oxidizing agent.

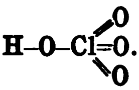
Chlorates are formed by conducting chlorine into hot, concentrated solutions of alkalies to complete saturation. With potassium hydroxide the equation is, —

$$6\ KOH + 3\ Cl_2 \longrightarrow KClO_3 + 5\ KCl + 3\ H_2O.$$

The *chlorate* is separated from the *chloride* by recrystallization from hot water. The potassium chlorate, being much less soluble than the other, separates out first.

Potassium chlorate has already been used to produce oxygen (§ 19). The equations representing the action of hydrochloric acid upon potassium chlorate (§ 82) are, in part, —

$$(1)\ KClO_3 + HCl \longrightarrow KCl + HClO_3;$$
$$(2)\ HClO_3 + 5\ HCl \longrightarrow 3\ H_2O + 3\ Cl_2.$$



282. Perchloric Acid, $H{-}O{-}Cl\begin{matrix}\nearrow O\\ =O\\ \searrow O\end{matrix}$. — Perchloric acid is a colorless, explosive liquid about 1.8 times as heavy as water. Its salts, the *perchlorates*, are produced when the chlorates are partly decomposed by heat.

In the decomposition of potassium chlorate (*cf.* § 19), a point is soon reached at which a considerable increase of temperature is needed to continue the evolution of oxygen. The amount of oxygen evolved up to this point is only *one-third* of the quantity present in potassium chlorate. If we stop at this stage, we obtain a mixture of *potassium perchlorate* and *potassium chloride*, as shown in the equation,

$$2\,KClO_3 = KClO_4 + KCl + O_2.$$

The potassium chloride is much more soluble than the perchlorate; hence these substances may be separated by recrystallization from water.

283. Compounds of Bromine with Oxygen and Hydrogen. — No compounds of bromine and oxygen have been prepared in a pure condition. With oxygen and hydrogen bromine forms *hypobromous acid*, *bromic acid*, and *perbromic acid.*

The graphic formulas of these acids are like those of the corresponding chlorine compounds.

Hypobromites are formed when cold, dilute alkalies are treated with bromine, but with *less* than is required for saturation.

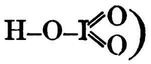
$$2\,KOH + 2\,Br \longrightarrow KOBr + H_2O + KBr.$$

The hypobromites, like the hypochlorites, are *oxidizing* agents.

Bromates are formed when *hot* alkalies are saturated with bromine (*cf.* chlorates, § 281). Potassium bromate is a white, crystalline solid like potassium chlorate. Heat decomposes it into potassium bromide and oxygen.

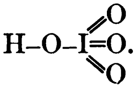
$$2\ KBrO_3 = 2\ KBr + 3\ O_2.$$

284. Compounds of Iodine with Oxygen and Hydrogen. — Two oxy-acids of iodine are known; they are *iodic* and *periodic* acids.

Iodic acid (HIO_3 or, *graphically*,  $\text{H–O–I}\begin{smallmatrix}=O\\=O\end{smallmatrix}$) is formed by oxidizing iodine with concentrated nitric acid. It is a crystalline solid. At 170° C. it breaks up into iodine pentoxide (I_2O_5) and water.

Iodates are formed by adding iodine to hot, concentrated solutions of alkalies. With potassium hydroxide the equation is, —

$$6\ KOH + 6\ I \longrightarrow KIO_3 + 5\ KI + 3\ H_2O.$$

Periodic acid is HIO_4, or  $\text{H–O–I}\begin{smallmatrix}=O\\=O\\=O\end{smallmatrix}$. Its salts are *periodates*, e. g., sodium periodate, $NaIO_4$.

285. The Halogen Family. — From the preceding pages it is evident that there is a great similarity in the properties of the elements *fluorine*, *chlorine*, *bromine*, and *iodine*. The close relation of these elements to one another is yet more marked if we consider that there is a *gradation* in the properties of these elements *in the order of the atomic masses.* Thus, the melting temperatures, the boiling temperatures, and the specific gravities of these elements *rise* from fluorine (atomic mass 19) to iodine (atomic mass 127). The intensity of the color of these elements also increases with the atomic mass: *fluorine* is greenish yellow; *chlorine*, green; *bromine*, brown; and *iodine*, black.

The gradation observed in their *physical* properties is true also of their *chemical* properties. Thus, the elements of *lower* atomic mass can expel those of *higher* atomic mass from their soluble metal salts.

The same gradation of properties is noticed in the *compounds* of the halogens. Thus, the *specific gravity* of the hydrogen compounds *increases* from hydrofluoric acid to hydriodic acid; while the *stability* of these compounds *decreases* in the same order.

In the case of the compounds of the halogens with oxygen, and with oxygen and hydrogen, the order of stability is reversed, iodine forming the *most* stable ones, chlorine very *unstable* ones, and fluorine none at all.

The same gradation of *color* seen in the elements themselves appears in many of their compounds. Thus, silver chloride is *white;* silver bromide, *light yellow;* silver iodide, *bright yellow.*

Some of the above (and other) facts appear in the following table: —

PROPERTIES.	FLUORINE.	CHLORINE.	BROMINE.	IODINE.
Atomic Mass	19	35.5	80	127
Boiling Temperature	—187° C.	—33°	+59°	+184°
Specific Gravity . .	1.15 (liquid)	1.5 (liquid)	3.2 (liquid)	5 (solid)
Union with Hydrogen takes place .	In the dark at ordinary temperatures.	In sunlight.	At red heat.	At red heat, but incompletely.
Heat of formation of Hydrogen Compound	37.6 heat units.	22	8	—6.1
Stability of Hydrogen Compound . .	Most stable.	Decomposed at 1500° C.	Decomposed at 800° C.	Decomposed at 180° C.
Stability of Oxygen Compound	Forms none.	Unstable.	Forms none.	Most stable.

A group of elements related to one another like the halogens is called a "**Natural Family of Elements.**" Several other natural families exist, and will be referred to later.

286. Exercises.

1. How many grams of bromine can be made from 150 grams of potassium bromide by using manganese dioxide and dilute sulphuric acid?
2. Calculate the per cent of hydrogen in hydriodic acid. In hydrobromic acid.
3. How would you separate a mixture of iodine and sand?

4. How could you distinguish, by chemical means, between a chloride, a bromide, and an iodide?

5. How could you identify a fluoride, *e. g.* calcium fluoride?

6. About how much would a liter of air weigh at +273° C. and 760 mm. pressure? A liter of iodine vapor?

The peculiar *instability* of ozone is due to the fact that the change from oxygen to ozone is accompanied by *absorption* of heat. In the presence of a substance capable of taking up oxygen, the ozone molecule readily gives up an atom of oxygen, and thus reverts to *molecular* oxygen, $O = O$.

288. Properties of Ozone. — As might be expected, the *oxidizing* power of ozone is very great. Moist phosphorus and sulphur are converted by it into phosphoric and sulphuric acids, respectively; and ammonia is at once oxidized to nitric acid. Organic coloring substances, *e. g.* indigo and litmus, are at once decolorized by ozone. The bleaching of fabrics on exposure to the air is probably due to the action of ozone present in the air.

When ozone is heated, its molecule is decomposed, and ordinary oxygen results. The reversion of ozone to oxygen is accompanied by an *expansion* of volume just equal to the contraction that takes place when oxygen changes into ozone.

Ozone is readily absorbed by oil of turpentine; hence the amount of ozone formed in a given volume of oxygen may be determined by exposing the *ozonized* oxygen to this substance. Only about *six per cent* of a given amount of oxygen can be converted into ozone, because the reverse change of ozone into oxygen soon produces a condition of equilibrium.

The presence of ozone in ozonized air is readily detected by means of a mixture of potassium iodide and starch paste — best upon a piece of filter paper. The ozone sets iodine free, probably according to the equation,

$$2\,KI + H_2O + O_3 \longrightarrow 2\,KOH + 2\,I + O_2.$$

289. Hydrogen Peroxide. — Closely related to ozone, and long confused with it, is *hydrogen peroxide*, H_2O_2. Hydrogen peroxide is a colorless liquid about one and one-half times as heavy as water; it possesses remarkable oxidizing and reducing powers.

A dilute solution of hydrogen peroxide may be made by adding *barium peroxide*, BaO_2, to dilute hydrochloric acid. The equation is, —

$$BaO_2 + 2\ HCl \longrightarrow BaCl_2 + H_2O_2.$$

A somewhat better way is to treat a dilute solution of tartaric acid with sodium peroxide, Na_2O_2.

$$Na_2O_2 + H_2C_4H_4O_6 = Na_2C_4H_4O_6 + H_2O_2.$$

Sodium peroxide is made (along with sodium monoxide, Na_2O) by burning sodium in air or oxygen.

When phosphorus is partly immersed in water, it acts upon the moist air to form both hydrogen peroxide and ozone. Both of these substances are formed, also, by holding a hydrogen flame against a piece of ice.

Hydrogen peroxide is formed in the electrolysis of water, if oxygen is passed into the water at the negative (—) electrode. The oxygen is reduced by the nascent hydrogen evolved at the electrode.

Hydrogen peroxide is found in the air, and in all rain water and snow.

290. Properties of Hydrogen Peroxide. — Hydrogen peroxide may be obtained almost pure by distilling a dilute aqueous solution of it at low pressure. The apparatus for distilling at reduced pressure is essentially as shown in Fig. 57.

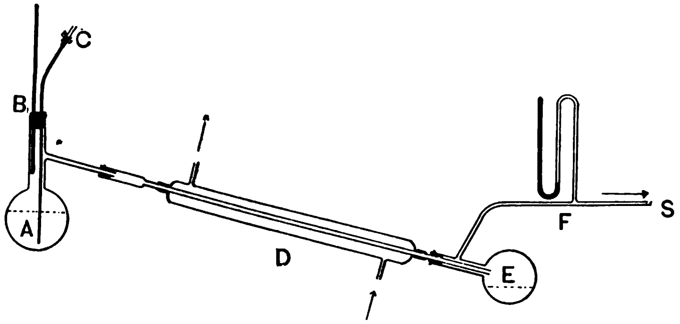


FIG. 57.

A distilling flask (A) is provided with a thermometer (B) and a capillary tube (C). The capillary tube allows a very small stream of air to be drawn through the apparatus. The distilling flask is connected *air-tight* with the condenser (D) and the receiver (E). The pressure, in millimeters of mercury, is indicated by the *manometer* (F). The air is exhausted at S by a water or mercury suction-pump.

At 26 mm. pressure hydrogen peroxide boils at 69° C.; under the same pressure water boils at 27° C.; hence the two substances can be separated readily. The aqueous solution of hydrogen peroxide has a bitter taste and produces white spots upon the skin. It is a powerful antiseptic.

Hydrogen peroxide decomposes readily, especially in the presence of *basic* substances. The products are water, and oxygen in the nascent condition; hence hydrogen peroxide is a powerful oxidizing agent. It decolorizes indigo, litmus, etc., as ozone does. It at once oxidizes hydrochloric acid to water and chlorine.

Hydrogen peroxide acts also as a *reducing* agent *with evolution of oxygen.* Thus, it reduces mercuric oxide to mercury and sets oxygen free.

$$HgO + H_2O_2 \longrightarrow Hg + O_2 + H_2O.$$

One atom of each oxygen molecule (O_2) comes from the hydrogen peroxide, and the other from the oxide reduced.

Potassium permanganate solution is at once decolorized by hydrogen peroxide, and potassium chromate and bichromate solutions are changed to a green color. All of these are *reductions.*

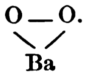
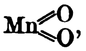
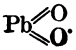
Ozone and hydrogen peroxide *reduce* each other.

$$O_3 + H_2O_2 \longrightarrow O_2 + H_2O + O_2.$$

Hydrogen peroxide, like ozone, decomposes with *evolution* of heat; this fact accounts for its instability.

The *common test* for the presence of hydrogen peroxide in a solution is to add to the solution in a test tube about two or three cubic centimeters of ether, and then *one drop* of potassium bichromate solution. When the test tube is shaken, the layer of ether is colored a beautiful blue, if hydrogen peroxide is present.

291. Composition of Hydrogen Peroxide. — Hydrogen peroxide is composed of 1.01 parts, by weight, of hydrogen to every 16 parts of oxygen. Its molecular mass is 34; hence its formula is H_2O_2. The graphic formula of hydrogen peroxide is H–O–O–H.

The effect of the *structure* of the molecule, *i. e.*, the way in which the atoms are united, upon the properties of substances, is admirably illustrated by the differences in the behavior of the two classes of *dioxides*. Thus, while *calcium peroxide* (CaO_2), *sodium peroxide* (Na_2O_2), and *barium peroxide* (BaO_2) give hydrogen peroxide when treated with dilute acids, *lead dioxide* (PbO_2) and manganese dioxide (MnO_2) do not. The structure of all *true* peroxides is like that of hydrogen peroxide. The graphic formula of sodium peroxide is, therefore, $Na - O - O - Na$, and that of barium peroxide,  $\begin{array}{c} O - O \\ \diagdown \ \diagup \\ Ba \end{array}$. The graphic formula of the *dioxides* is different, that of *manganese dioxide* being, probably,  $\mathrm{Mn}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown\!\!\diagdown O}$, and that of *lead dioxide*  $\mathrm{Pb}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown\!\!\diagdown O}$.

CHAPTER XIX.

THE NITROGEN FAMILY.
PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH.

A. Phosphorus.

292. Occurrence and Preparation of Phosphorus. — Phosphorus is found in nature only in the combined form, chiefly in *phosphates.* The most abundant phosphate is calcium phosphate, $Ca_3(PO_4)_2$. Calcium phosphate exists in the soil, and is taken up from it by plants. Animals consume phosphates in their food.

The immediate source of most phosphorus is *bone-ash,* which contains about 60% to 70% of its weight of calcium phosphate. The present process of making phosphorus is to heat calcium phosphate with *charcoal* and *sand* in the electric furnace.

We can understand the chemical reactions involved in making phosphorus by considering them separately.

(1) The calcium phosphate probably breaks up in the presence of the silica (sand) into *quicklime* and *phosphorus pentoxide.*

$$Ca_3(PO_4)_2 \longrightarrow 3\ CaO + P_2O_5.$$

(2) The silica and quicklime unite to give *calcium silicate.*

$$3\ CaO + 3\ SiO_2 = 3\ CaSiO_3.$$

(3) The charcoal reduces the phosphorus pentoxide to phosphorus.

$$P_2O_5 + 5\ C \longrightarrow 2\ P + 5\ CO.$$

Hence the *complete* equation is, —

$$Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C = 3\ CaSiO_3 + 5\ CO + 2\ P.$$

The phosphorus escapes from the furnace as a vapor, and is collected under water. To purify it, it is redistilled and pressed in the liquid state (under water) through a bone-ash filter. The phosphorus thus obtained is a white and transparent solid. About three thousand tons of phosphorus are made every year.

293. Properties. — Phosphorus, like *sulphur*, exists in several allotropic forms with widely differing properties. Ordinary or *yellow* phosphorus has a specific gravity of about 1.8, melts at about 45° C., and boils at 287° C. It is insoluble in water, but dissolves readily in *carbon disulphide*, CS_2.

Phosphorus derives its name, which means "bearer of light" (*cf.* Latin, *lucifer*), from its property of *phosphorescing*, i. e., glowing, when exposed in the dark to moist air or other gases containing oxygen. This phenomenon is caused by slow combustion on the surface of the phosphorus.

Ordinary phosphorus ignites in air at 40° C., and burns with a hot flame to phosphorus *trioxide* and *pentoxide*.

$$4\ P + 3\ O_2 = 2\ P_2O_3.$$
$$4\ P + 5\ O_2 = 2\ P_2O_5.$$

The spontaneous ignition of finely divided phosphorus has already been described (*cf.* § 29).

Phosphorus unites readily with chlorine, bromine, and iodine even at the ordinary temperature. Two compounds of phosphorus and chlorine are possible, viz., the *trichloride*, PCl_3, and the *pentachloride*, PCl_5. Phosphorus trichloride is a liquid; phosphorus pentachloride, a crystalline solid.

$$2\,P + 3\,Cl_2 = 2\,PCl_3.$$
$$2\,P + 5\,Cl_2 = 2\,PCl_5.$$

Yellow phosphorus is *very poisonous.*

294. Red Phosphorus. — A great difference exists between yellow phosphorus and the *red* modification. Red phosphorus is a reddish powder 2.2 times as heavy as water, infusible at red heat, unable to phosphoresce, insoluble in carbon disulphide, and not poisonous. It ignites at about 260° C. in air. Red phosphorus unites with the halogens only when heated.

Red phosphorus is prepared by heating the ordinary form in closed iron tubes to 300° C. A small amount of the yellow phosphorus remains unchanged; this is removed by means of carbon disulphide, in which the red variety is insoluble.

When a given amount of red phosphorus is burned, there is much less heat liberated than with an equal amount of the *yellow* form; the red has therefore much less energy than the yellow. This statement agrees with the known fact that when yellow phosphorus is changed into the red there is an *evolution* of heat.

295. Molecular Mass of Phosphorus. — The weight of a liter of phosphorus in the vapor condition is almost four times that of a liter of oxygen at the same temperature and pressure; consequently the molecular mass of phosphorus, as a vapor, must be about 124, that is, about four times the atomic mass. This can be due only to the fact that the molecule of phosphorus in the gaseous condition contains *four* atoms. The molecular formula of phosphorus vapor is thus written P_4, just as that of oxygen is O_2.

296. Matches. — Most of the phosphorus that is made is used to *tip* matches. The ordinary friction match, as made at present, consists of a splint of wood tipped, *first*, with sulphur, and *then* with a mixture containing some oxidizing agent, phosphorus, and an adhesive substance, like glue. The oxidizing agent may be *potassium nitrate* or *chlorate*, or the oxide of lead known as *red lead*, which has the formula Pb_3O_4.

The chemical operations involved in lighting a match are essentially as follows: —

(1) The heat generated by rubbing the tip of the match against a rough surface causes the phosphorus to combine with the oxygen of the oxidizing agent in immediate contact with it.

(2) The combustion of the phosphorus causes the sulphur to be raised to the kindling temperature of sulphur.

(3) The burning of the sulphur raises the temperature of the wood to the kindling point; *and the match burns.*

Safety matches have not the property of being easily ignited when rubbed; they require contact with a specially prepared surface. This surface is usually on the side of the match box, and consists of red phosphorus mixed with sand. The *tip* of the safety match generally contains antimony trisulphide (Sb_2S_3), an oxidizing agent, and glue.

297. Hydrogen Phosphide (PH_3). — Hydrogen phosphide, or *phosphine*, is a colorless gas which, as ordinarily made, is *spontaneously combustible*. The *common method* of preparing it is to heat a mixture of yellow phosphorus and a strong solution of *sodium hydroxide*. The equation is, —

$$4\,P + 3\,NaOH + 3\,H_2O \longrightarrow \underset{\text{sodium hypophosphite.}}{3\,NaH_2PO_2} + PH_3.$$

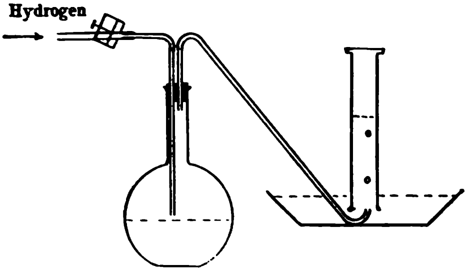


FIG. 58.

The apparatus (Fig. 58) consists of a generating flask containing the phosphorus and the sodium hydroxide solution. The stopper of the flask has two holes, one for a tube from a hydrogen generator and the other for a delivery tube ending under water. The air of the apparatus is first washed out by means of hydrogen (or illuminating gas) ; the gas is then cut off and the flask is heated. The escaping phosphine may be collected in a receiver, as shown in the figure, and this exposed to the air, or the bubbles of the gas may be allowed to escape through the water directly into the air. The material of the white smoke formed when phosphine burns is *phosphorus pentoxide*, *water*, and *phosphoric acid*.

The equation for the combustion of phosphine is, —

$$2\ PH_3 + 4\ O_2 \longrightarrow P_2O_5 + 3\ H_2O.$$

Pure phosphine is not actually ignited until its temperature reaches 100° C. As the gas is ordinarily prepared, however, it contains small amounts of the vapor of another phosphide of hydrogen (P_2H_4), which *is* spontaneously combustible, and which, therefore, ignites the phosphine.

298. Phosphonium Salts. — Phosphine may be regarded as *ammonia*, NH_3, with its nitrogen replaced by phosphorus. Although similar to ammonia in composition, phosphine is much less *basic*. The aqueous solution of phosphine is not alkaline at all; the compound PH_4OH can hardly be present in the solution.

Phosphine can, however, be made to unite with the *halogen acids*. The compounds thus formed correspond with the *ammonium* salts of the halogens; hence they are called *phosphonium* salts. *Phosphonium bromide* (PH_4Br) and *phosphonium iodide* (PH_4I) are much like *ammonium* bromide and iodide, respectively.

Phosphonium iodide is decomposed by soluble hydroxides, much as ammonium chloride is (*cf.* § 142). This fact is evident from the equations,

$$NH_4Cl + KOH \longrightarrow KCl + NH_4OH \text{ (}i.\ e.\text{, } NH_3 + H_2O\text{)};$$
$$PH_4I + KOH \longrightarrow KI + PH_3 + H_2O.$$

299. Phosphides. — The phosphides of the metals may be considered derivatives of *hydrogen phosphide*, just as *sulphides* are of *hydrogen sulphide*. The formula of *calcium phosphide* is Ca_3P_2; of *silver phosphide*, Ag_3P

Calcium phosphide is a white solid; when it is treated with water or with hydrochloric acid, it gives off hydrogen phosphide. The equation resembles that for the action of hydrochloric acid upon ferrous sulphide. Both equations are given.

$$Ca_3P_2 + 6\ HCl \longrightarrow 3\ CaCl_2 + 2\ PH_3.$$
$$FeS + 2\ HCl \longrightarrow FeCl_2 + H_2S.$$

300. Oxides of Phosphorus. — Two common oxides of phosphorus are known, viz., the *trioxide* (P_2O_3) and the pentoxide (P_2O_5). Both are white solids.

The weight of a given volume of phosphorus trioxide in the gaseous state is known to be *twice* that demanded by the formula P_2O_3; consequently it is better to write the formula P_4O_6.

Phosphorus pentoxide is formed when phosphorus burns in air or oxygen *free from moisture.*

$$4\ P + 5\ O_2 = 2\ P_2O_5.$$

It is a bulky, white solid which has great attraction for moisture; when put into water it hisses like hot iron. The product is *metaphosphoric acid*, HPO_3.

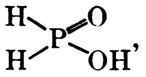
$$P_2O_5 + H_2O = 2\ HPO_3.$$

Phosphorus pentoxide has been referred to as capable of decomposing anhydrous nitric acid and producing *nitrogen pentoxide* (*cf.* § 166). It is the *anhydride* of metaphosphoric acid, as nitrogen pentoxide is of nitric acid.

301. Oxygen Acids of Phosphorus. — Several compounds of phosphorus with oxygen and hydrogen are known. Three of these form a series like the oxygen acids of chlorine (*cf.* §§ 106 and 278); they are, —

Hypophosphorous acid, H_3PO_2;
Phosphorous acid, H_3PO_3;
Phosphoric acid, H_3PO_4.

302. Hypophosphorous Acid. — Attention has already been called to the fact that when phosphorus acts upon sodium hydroxide (*cf.* § 297) it produces *sodium hypophosphite* (NaH_2PO_2) as well as phosphine. With barium hydroxide, *barium hypophosphite*, $Ba(H_2PO_2)_2$, is produced.

The hypophosphites are salts of hypophosphorous acid. This is a *monobasic* acid (*cf.* § 105). Its graphic formula is , only the hydrogen atom attached to oxygen being ordinarily replaceable by metals.

Hypophosphorous acid is a powerful *reducing agent*, owing to the ease with which it goes over into phosphoric acid.

$$H_3PO_2 + O_2 = H_3PO_4.$$

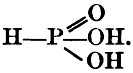
303. Phosphorous Acid. — Phosphorous acid is an intermediate product in the oxidation of hypophosphorous acid. It is itself a reducing agent, owing to its ready oxidation to phosphoric acid. Its *anhydride* is phosphorus trioxide, P_2O_3.

$$P_2O_3 + 3\ H_2O = 2\ H_3PO_3.$$

Phosphorous acid may be prepared by treating *phosphorus trichloride* or *tribromide* with water (*cf.* § 271).

$$PCl_3 + 3\ H_2O \longrightarrow H_3PO_3 + 3\ HCl.$$

Ordinary phosphorous acid is *dibasic ;* its graphic formula is, therefore,



$$H\text{—}P\begin{matrix} \diagup\!\!\diagup O \\ \text{—}OH \\ \diagdown OH \end{matrix}.$$

304. The Phosphoric Acids. — The three phosphoric acids are, (1) *orthophosphoric acid*, or simply *phosphoric acid* (H_3PO_4); (2) *pyrophosphoric acid* ($H_4P_2O_7$), and (3) *metaphosphoric acid* (HPO_3).

There is still another phosphoric acid, from which all of the three named may be supposed to be derived, *by loss of water ;* this is *normal* phosphoric acid, $P(OH)_5$. It corresponds to *normal* nitric acid, $N(OH)_5$. But while the ordinary form of nitric acid is HNO_3, *i. e.*, the molecule of the normal acid minus *two* molecules of water, the phosphoric acid from which the phosphates are chiefly derived is the *orthophosphoric acid*, H_3PO_4. The molecule of this acid is the molecule of the *normal* acid minus only *one* molecule of water:

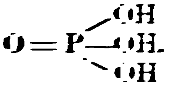
$$P(OH)_5 - H_2O = H_3PO_4.$$

If the molecule of orthophosphoric acid loses a molecule of water, we have *metaphosphoric acid*, HPO_3. This acid corresponds to nitric acid, HNO_3.

Pyrophosphoric acid is derived from orthophosphoric acid by loss of *one* molecule of water from two molecules of the orthophosphoric acid.

$$2\,H_3PO_4 - H_2O = H_4P_2O_7.$$

The *complete anhydride* of all the phosphoric acids is *phosphorus pentoxide*, P_2O_5.

Orthophosphoric acid is *tribasic*, a fact expressed in its graphic formula,  $O = P\begin{smallmatrix}-OH\\-OH\\-OH\end{smallmatrix}$. It therefore forms two *acid* salts (*cf.* § 103) and a *normal* salt.

Thus, with sodium hydroxide we may get,—
(1) Sodium di-hydrogen phosphate, NaH_2PO_4;
(2) Disodium hydrogen phosphate, Na_2HPO_4;
(3) Trisodium phosphate, Na_3PO_4.

Salts like the *first* of these, in which only *one-third* of the hydrogen is replaced, are called *primary* phosphates; those in which *two-thirds* of the hydrogen is replaced are called *secondary* phosphates. The normal salts are *tertiary* phosphates.

305. Preparation of the Phosphoric Acids.—The best way to obtain *orthophosphoric acid* is to treat red phosphorus with nitric acid, and to evaporate the resulting solution. At the ordinary temperature the acid consists of colorless, deliquescent crystals.

Pyrophosphoric acid is best made by heating the *ortho-* acid for some time to 260° C.; the *meta-* acid is made by heating the *ortho-* or the *pyro-* acid to 300° C.

Metaphosphoric acid always results when phosphorus pentoxide dissolves in water.

$$P_2O_5 + H_2O = 2\ HPO_3.$$

When the *meta-* acid is boiled with water it goes over into the *ortho-* acid.

$$HPO_3 + H_2O = H_3PO_4.$$

306. Salts of the Phosphoric Acids. — *Metaphosphates* are obtained from *primary orthophosphates only*, by the loss of *one* molecule of water from every molecule of the orthophosphate.

Thus, sodium metaphosphate, $NaPO_3$, is obtained by heating sodium di-hydrogen phosphate.

$$NaH_2PO_4 = H_2O + NaPO_3.$$

The so-called "*metaphosphate bead*" is made by heating either sodium di-hydrogen phosphate or sodium ammonium hydrogen phosphate upon a loop of platinum wire. Sodium ammonium hydrogen phosphate (also called "microcosmic salt") has the formula $NaNH_4HPO_4$. When heated it first loses ammonia, like any ammonium salt of a "*fixed*" acid, giving sodium di-hydrogen phosphate. This then loses water.

$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O.$$

When a *secondary* orthophosphate, *e. g.*, Na_2HPO_4, loses water, one molecule of water must come from *two* molecules of the phosphate; hence a *pyrophosphate* results.

$$2\ Na_2HPO_4 - H_2O = Na_4P_2O_7 \text{ (sodium pyrophosphate).}$$

307. Uses of the Phosphates. — A knowledge of the relations between the phosphates is essential to an understanding of the reactions involved in making fertilizers and phosphorus.

The phosphate found in bone-ash and in nature is normal calcium phosphate, $Ca_3(PO_4)_2$. This, however, is *insoluble* in water. To convert it into soluble form for the use of plants, the normal phosphate is treated with sulphuric acid. This changes it into *primary* calcium phosphate, $Ca(H_2PO_4)_2$, which is soluble.

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow 2\ CaSO_4 + Ca(H_2PO_4)_2.$$

Calcium sulphate is much less soluble in water than the primary calcium phosphate ; hence the two can be separated readily.

The primary phosphate of calcium is used not only as a fertilizer, but also in making *baking powders* (*cf.* § 206) and as a *source* of phosphorus.

The *old* process of making phosphorus from a phosphate consists, (1) in changing the phosphate into *metaphosphate*, and (2) in *reducing* the metaphosphate.

The change of primary *calcium* phosphate, like that of the *sodium* salt, into metaphosphate, takes place on heating.

$$Ca(H_2PO_4)_2 = Ca(PO_3)_2 + 2\ H_2O.$$

The reduction of calcium metaphosphate to phosphorus takes place when the metaphosphate is heated with charcoal or with charcoal and silica, SiO_2 (*cf.* § 292).

B. Arsenic.

308. Occurrence and Preparation of Arsenic. — The element arsenic is found in nature both free ar[illegible]d combined. Its chief ores are *realgar* and *orpime*[illegible] (As_2S_2 and As_2S_3, respectively), the *oxide* (As_2O_3), an[illegible] *arsenopyrite* (FeAsS). Arsenopyrite is iron pyrit[illegible] (FeS_2) with half of the sulphur replaced by arsenic.

The element may be prepared by reducing the oxid[illegible] with charcoal.

$$As_2O_3 + 3\ C \longrightarrow 2\ As + 3\ CO.$$

309. Properties of Arsenic. — Arsenic forms compounds which correspond closely with the compounds of phosphorus. The element itself is, however, more metallic than phosphorus. It exists in at least *two* allotropic forms.

The ordinary form of arsenic is gray, has a crystalline structure, and is about 5.7 times as heavy as water. It is not at all malleable, but, on the contrary, crumbles to powder when struck.

When arsenic is heated to about 500° C. out of contact with the air, it *sublimes*, forming a yellow vapor. By comparing the weight of a known volume of this vapor with that of oxygen under the same conditions, it is found that the molecular mass of arsenic vapor is about 300. The atomic mass being 75, the molecule must contain *four* atoms ; hence the molecular formula is As_4. Above 1,700° C., however, most of the molecules containing four atoms *dissociate* into simpler molecules of *two* atoms each, *i. e.*, As_2 molecules.

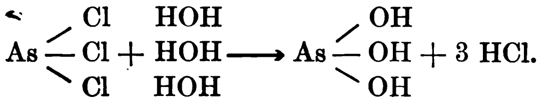
Arsenic begins to burn at about 180° C. to form arsenic trioxide, As_2O_3. The flame is bluish-white. Like phosphorus and antimony, arsenic unites with chlorine at the ordinary temperature to form the chloride, $AsCl_3$.

$$2\ As + 3\ Cl_2 = 2\ AsCl_3.$$

The same substance is formed when arsenic trioxide, As_2O_3, is treated with concentrated hydrochloric acid solution.

$$As_2O_3 + 6\ HCl \longrightarrow 2\ AsCl_3 + 3\ H_2O.$$

Arsenic trichloride is a colorless liquid; it is decomposed by an *excess* of water, giving *arsenious acid* and hydrochloric acid.



$$\mathrm{As}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + \begin{matrix}\mathrm{HOH}\\ \mathrm{HOH}\\ \mathrm{HOH}\end{matrix} \longrightarrow \mathrm{As}\begin{matrix}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{matrix} + 3\ \mathrm{HCl}.$$

Arsenic trichloride is thus like *phosphorus* trichloride, which with water gives phosphorous acid and hydrochloric acid (*cf.* § 303).

310. Hydrogen Arsenide. — Arsenic combines with nascent hydrogen to form ***hydrogen arsenide*** or *arsine*, AsH_3, a substance which corresponds with phosphine gas, PH_3. Arsine cannot, however, be made to unite with hydrobromic acid, etc., to give compounds resembling ammonium and phosphonium salts (*cf.* § 298).

The most common method of getting arsine (mixed with hydrogen) is to add an arsenic compound to a flask in which hydrogen is being generated; the nascent hydrogen unites with the arsenic of the compound.

Marsh's Test. — Advantage is taken of the properties o arsine to test for the presence of arsenic in any substance; th test is known as *Marsh's test.*

To a flask in which pure hydrogen is being generated (Fig 59), there is attached a calcium chloride tube and a hard glas

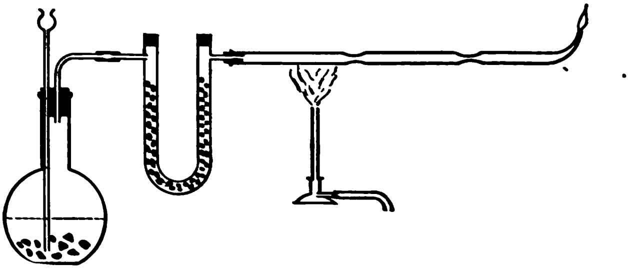


FIG. 59.

tube drawn out as shown in the figure. The hydrogen is allowed to pass off until the usual test (*cf.* p. 13) shows that all air has been removed. The jet of hydrogen is now lighted, and a few drops of the liquid to be tested for arsenic are added through the thistle-tube. If arsenic is present, the flame changes to a bluish-white color, and a cold piece of porcelain held in the flame receives a shiny, black deposit, called an "arsenic mirror."

If the hard glass tube is heated, the arsine passing through it is decomposed, and an arsenic mirror appears in the tube. Here the arsenic may be identified by passing hydrogen sulphide, H_2S, through the heated tube. The same precautions must be taken to have all air removed as in the case of hydrogen. Hydrogen sulphide changes the arsenic into *arsenic trisulphide*, As_2S_3; this is a golden-yellow solid called *orpiment* (from *auri pigmentum*). If, now, dry hydrochloric acid gas is passed through the tube, the arsenic trisulphide does not change. These properties serve to distinguish between the arsenic mirror and that of *antimony* (*cf.* § 318).

311. Arsenic Trioxide. — The oxides of arsenic are the *trioxide* (As_2O_3) and the pentoxide (As_2O_5); these correspond to the phosphorus oxides. Arsenic trioxide (often called "arsenic" or "white arsenic") is the most common arsenic compound. It is a white powder which sublimes, without melting, at about 220° C. The vapor has a garlic odor. When the vapor solidifies, the arsenic trioxide appears in the form of a transparent mass. At very high temperatures the molecule of the vapor is represented by As_2O_3; but between 220° and 700° C. the molecules are *doubled*, and the formula is As_4O_6.

Uses. — Arsenic trioxide is used in medicine and as a poison. Its poisonous action upon the human system is rather slow, owing to its dissolving only slowly in the liquid of the stomach. The antidote is a mixture of ferric hydroxide [$Fe(OH)_3$] and magnesia (MgO).

The people of certain mountain districts are addicted to the use of arsenic trioxide because it enables them to breathe more easily when climbing. By beginning with very small quantities and gradually increasing the dose, they are able to take much more than the lethal dose without injury. But the difficulty comes when they try to leave off the habit: for they then suffer all the effects of arsenic poisoning.

312. Arsenious Acid. — Arsenic trioxide is slightly soluble in water; the solution probably contains *arsenious acid*, H_3AsO_3.

$$As_2O_3 + 3\ H_2O = 2\ H_3AsO_3.$$

Arsenious acid is not known in the free state because it breaks up into arsenic trioxide (its anhydride) and water. The salts of arsenious acid are called *arsenites*. Solutions of these are formed when arsenic trioxide is treated with alkalies. Thus, sodium hydroxide and arsenic trioxide (with water this is *arsenious acid*) form *sodium arsenite*, Na_3AsO_3.

$$H_3AsO_3 + 3\ NaOH \longrightarrow Na_3AsO_3 + 3\ H_2O.$$

Many arsenites are derived from *metarsenious acid*, $HAsO_2$, which may be looked upon as arsenious acid *minus* water.

$$H_3AsO_3 = HAsO_2 + H_2O.$$

Sodium metarsenite would be $NaAsO_2$.

Double Nature of Arsenious Acid. — Arsenic trioxide (or arsenious acid) reacts not only with alkalies, giving arsenites and water, but also with acids, giving *arsenic salts* and water. Thus, with concentrated hydrochloric acid and arsenic trioxide, we get arsenic trichloride and water.

$$As_2O_3 + 6\ HCl \longrightarrow 2\ AsCl_3 + 3\ H_2O; \text{ or,}$$
$$H_3AsO_3 + 3\ HCl \longrightarrow AsCl_3 + 3\ H_2O.$$

Arsenious acid has thus a *double* nature; for toward strong bases it acts like an acid, forming with the base an *arsenite;* while toward a strong acid it acts like a base, giving with the acid a *salt* and water. Arsenic is, in fact, *intermediate* between the non-metals and the metals.

Arsenic Greens. — At least two arsenic compounds have a bright green color; these are *copper arsenite*, called "Scheele's green" and a mixture of copper arsenite and copper acetate, called "Schweinfurt's green." Both of these are sold as "Paris green." These dyes were formerly used to color wall-paper, paints, etc. They are too dangerous, however, and are now rarely used as dyes. Paris green is used to destroy potato-bugs, etc.

313. Arsenic Acid. — Arsenic pentoxide, As_2O_5, is the anhydride of *arsenic acid*, H_3AsO_4.

$$As_2O_5 + 3\ H_2O = 2\ H_3AsO_4.$$

Arsenic acid is formed by dissolving arsenic or arsenic trioxide in concentrated nitric acid. (Compare the preparation of phosphoric acid from phosphorus, § 305.)

The arsenic acids have formulas of the same type as those of phosphorus: —

H_3AsO_4 is orthoarsenic acid;
$H_4As_2O_7$ is pyroarsenic acid;
$HAsO_3$ is metarsenic acid.

Metarsenic acid finally gives, by loss of water, arsenic pentoxide.

$$2\ HAsO_3 = H_2O + As_2O_5.$$

The *arsenates* are like the corresponding phosphates.

314. Arsenic Trisulphide. — When the solution of an arsenic compound is treated with hydrogen sulphide, a yellow precipitate is generally produced; this consists of either the trisulphide (As_2S_3) or the pentasulphide (As_2S_5). Both sulphides react with ammonium sulphide [$(NH_4)_2S$] and other soluble sulphides. The solution contains a *sulpharsenite* or *sulpharsenate.* Thus with sodium sulphide and arsenic trisulphide the equation is, —

$$3\ Na_2S + As_2S_3 = 2\ Na_3AsS_3.$$

The sulpharsenite (Na_3AsS_3) is simply an arsenite with its *oxygen* replaced by *sulphur.*

When the sulpharsenite is treated with a dilute acid, *e. g.*, hydrochloric acid, *sulpharsenious acid*, H_3AsS_3, is set free; this breaks up into hydrogen sulphide and arsenic trisulphide. Arsenic trisulphide, being insoluble, is reprecipitated. These facts are shown in the equations, —

$$Na_3AsS_3 + 3\ HCl \longrightarrow H_3AsS_3 + 3\ NaCl.$$
$$2\ H_3AsS_3 = 3\ H_2S + As_2S_3.$$

Ammonium sulpharsenite, $(NH_4)_3AsS_3$, undergoes a similar decomposition.

C. Antimony.

315. Preparation of Antimony. — Antimony is found in nature chiefly combined with sulphur in the mineral *stibnite*, Sb_2S_3. To obtain the element the sulphide is first *roasted*, i. e., heated in a stream of air, and then heated with charcoal.

Roasting converts the antimony sulphide into the *trioxide* (Sb_2O_3), or the tetroxide (Sb_2O_4), and sulphur dioxide.

$$2\ Sb_2S_3 + 9\ O_2 \longrightarrow 2\ Sb_2O_3 + 6\ SO_2\text{; or,}$$
$$Sb_2S_3 + 5\ O_2 \longrightarrow Sb_2O_4 + 3\ SO_2.$$

The reduction of either of these oxides by charcoal gives antimony and carbon monoxide.

$$Sb_2O_3 + 3\ C \longrightarrow 2\ Sb + 3\ CO.$$

316. Physical Properties. — Antimony is a solid having a bright, silvery luster which is not easily tarnished in air. Antimony is not malleable. At about 430° C. it melts to a liquid of a slightly higher specific gravity. When melted antimony solidifies it *expands* again; hence antimony is valuable as a constituent of materials for *casts*, such as type-metal. The specific gravity of the solid is 6.7. The specific gravity of the vapor shows that in the *gaseous* condition the formula of the molecule is Sb_2 (*cf.* §§ 295 and 300).

317. Chemical Properties. — Antimony burns in the air to form the trioxide or the tetroxide. It combines with chlorine to give antimony ***trichloride*** (*cf.* § 84) or the *pentachloride*, $SbCl_5$. With fluorine, bromine, and iodine it forms similar compounds.

Antimony is insoluble in hydrochloric acid. Nitric acid oxidizes it to antimony trioxide or ***antimonic acid***, H_3SbO_4.

$$4\ Sb + 3\ O_2 = 2\ Sb_2O_3.$$
$$4\ Sb + 5\ O_2 = 2\ Sb_2O_5.$$
$$Sb_2O_5 + 3\ H_2O = 2\ H_3SbO_4.$$

With *aqua regia* antimony reacts, giving ***antimony*** *trichloride*. When the solution is distilled it gives the trichloride as a liquid boiling at 223° C. This solidifies to a pasty mass called "butter of antimony."

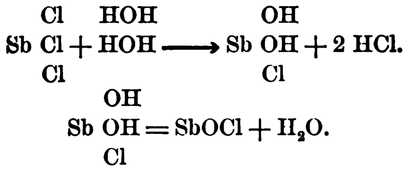
Concentrated sulphuric acid reacts with antimony. The products are shown in the equation,

$$2\ Sb + 6\ H_2SO_4 \longrightarrow \underset{\text{antimony sulphate}}{Sb_2(SO_4)_3} + 3\ H_2SO_3 + 3\ H_2O.$$

Antimony resembles arsenic and phosphorus on the one hand and bismuth on the other. It is like the former elements in the general structure of its compounds; like the latter in its ability to form a salt with sulphuric acid and in other *metallic* properties.

Its positive (+) properties are, however, ***weak***, as is indicated by the easy decomposition of its salts by water.

Thus, antimony trichloride is decomposed by much water, giving a *basic* chloride (its simplest formula is SbOCl) and hydrochloric acid.



$$\mathrm{Sb}\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix} + \begin{matrix}\mathrm{HOH}\\\mathrm{HOH}\\\ \end{matrix} \longrightarrow \mathrm{Sb}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\\\mathrm{Cl}\end{matrix} + 2\,\mathrm{HCl}.$$

$$\mathrm{Sb}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\\\mathrm{Cl}\end{matrix} = \mathrm{SbOCl} + \mathrm{H_2O}.$$

Again, although antimony trioxide reacts with *concentrated* sulphuric acid, giving antimony sulphate, $Sb_2(SO_4)_3$, yet when antimony trioxide reacts with the *dilute* acid, the product has the formula $(SbO)_2SO_4$. The compound SbOCl may be called *antimony oxy-chloride* or *antimonyl chloride*, the group SbO being called *antimonyl*. The compound having the formula $(SbO)_2SO_4$ is, therefore, *antimonyl sulphate.*

Antimony, even more than arsenic, is a *transition* element. Its oxide, Sb_2O_3, reacts not only with acids, giving antimony *salts*, but also with *alkalies*, giving salts of *antimony acids.* Thus, antimony trioxide gives with sodium hydroxide *sodium antimonite*, Na_3SbO_3. This is a salt of *antimonious acid*, which corresponds with phosphorous and arsenious acids.

318. Other Antimony Compounds. — Among the important antimony compounds are *hydrogen antimonide* (or *stibine*), *tartar emetic*, and *antimony trisulphide.*

Hydrogen antimonide, SbH_3, is formed from an antimony compound just as *hydrogen arsenide* is formed from an arsenic compound, namely, by reduction with *nascent* hydrogen (*cf.* § 310).

Marsh's test may be carried out with antimony in the apparatus used for arsenic (Fig. 59). When, however, hydrogen sulphide is passed over the antimony mirror, the antimony sulphide formed is *black*, while that of arsenic is *yellow*. Again, when hydrochloric acid gas is passed through the tube, the antimony sulphide forms drops of *antimony trichloride*, while the arsenic trisulphide is unchanged. We can thus distinguish between arsenic and antimony.

Tartar emetic is *potassium antimonyl tartrate*, $K.SbO.C_4H_4O_6$. It is formed by heating a mixture of antimony trioxide, potassium hydrogen tartrate (cream of tartar), and water. It is used in medicine.

Antimony trisulphide, Sb_2S_3, is formed by treating solutions of either antimonious salts or antimonites with hydrogen sulphide. Two isomeric antimony trisulphides are known. The one formed by precipitation is brick-red, while *stibnite* is black. The red form is unstable; it goes over into the black form *with evolution of heat*.

The precipitate of antimony trisulphide reacts readily with alkaline sulphides giving *sulphantimonites*, just as arsenic trisulphide gives *sulpharsenites* (*cf.* § 314). The sulphantimonites are decomposed by dilute acids; and antimony trisulphide is reprecipitated.

319. Uses of Antimony. — Antimony is used in making alloys. Examples are: printer's type-metal, pewter, and Britannia metal. *Antimony black* is a finely divided form of the metal; plaster casts are rubbed with it to give them a metallic coating.

D. Bismuth.

320. Preparation of Bismuth. — Bismuth is found in nature *free* and also in the form of the sulphide (Bi_2S_3)

and the oxide (Bi_2O_3). It is prepared from its sulphide as antimony is, namely, by first *roasting* the sulphide to form the oxide, and then *reducing* the oxide.

To get bismuth free from impurities, such as arsenic, etc., it is mixed with saltpeter and heated. The impurities are thus oxidized to compounds soluble in water, and can be separated from the bismuth.

321. Properties. — In its physical appearance bismuth is much like antimony, but it has a slightly *reddish* color. Its melting temperature is 265° C., and its specific gravity about 10.

Bismuth burns in the air when at red heat; the product is the trioxide, Bi_2O_3.

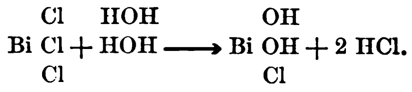
Bismuth trioxide is formed, also, by heating the nitrate $Bi(NO_3)_3$ (see § 169), and by heating the hydroxides $Bi(OH)_3$ and $BiO.OH$, which are produced when potassium hydroxide solution is added to a solution of a bismuth salt.

Unlike the trioxides of arsenic and antimony, bismuth trioxide has *not* the ability to react with alkalies to form salts. It is an entirely *basic* oxide. The higher oxide of bismuth, Bi_2O_5, has slightly acidic properties; for it is the anhydride of *bismuthic acid*, $HBiO_3$. The acid is, however, very weak and very unstable.

Bismuth forms no hydrogen compound corresponding to ammonia, phosphine, arsine, and stibine.

322. Bismuth Salts. — Bismuth combines with the halogens, giving tri-halogen compounds, which correspond to those of arsenic and antimony. It reacts with nitric acid to give the *nitrate*, $Bi(NO_3)_3$; with *aqua regia* to give the *chloride*, $BiCl_3$, and with concentrated sulphuric acid to give the sulphate, $Bi_2(SO_4)_3$.

Bismuth salts, like those of antimony, are decomposed by much water, giving the *basic salt* and free acid. The trichloride usually decomposes as follows: —



$$\mathrm{Bi}\begin{array}{l}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{array} + \begin{array}{l}\mathrm{HOH}\\\mathrm{HOH}\\\phantom{\mathrm{H}}\end{array} \longrightarrow \mathrm{Bi}\begin{array}{l}\mathrm{OH}\\\mathrm{OH}\\\mathrm{Cl}\end{array} + 2\,\mathrm{HCl}.$$

$$Bi(OH)_2Cl \longrightarrow BiO.Cl + H_2O.$$

The nitrate decomposes in a similar way.

When *hydrogen sulphide* is added to the solution of a bismuth salt there is produced an almost black precipitate of *bismuth sulphide*, Bi_2S_3. This is insoluble in alkaline sulphides.

323. Uses of Bismuth. — The principal use of bismuth is as an ingredient of alloys. Its chief alloys are *Wood's metal* and *Rose's metal.*

Wood's metal consists of *four* parts, by weight, of bismuth, *one* each of tin and cadmium, and *two* of lead. It melts at about 65° C.; hence it is much used for metal baths in the laboratory.

Rose's metal contains nine parts of bismuth to one each of lead and tin; it melts at 94° C.

The *basic nitrate* of bismuth (simplest formula, $BiO.NO_3$) is used in medicine under the name *bismuth sub-nitrate.*

324. The Nitrogen Family. — The elements nitrogen, phosphorus, arsenic, antimony, and bismuth, together with some *rare* elements, form a natural family, just as the halogens do; for in this, the nitrogen family, just as in the case of the halogens, we have a series of elements exhibiting a gradation of properties in the order of the atomic masses. The table on the next page shows this for some properties.

A complete list of the properties of the members of the nitrogen family will not agree so well as in the case of the halogens. When, however, we can compare corresponding compounds having the same number of atoms to the molecule, a fair degree of regularity exists.

325. Exercises.

1. What means are there of kindling fires without the use of phosphorus?

2. How much phosphorus is there in 440 grams (about one pound) of bone-ash, if 70% of the ash is calcium phosphate, $Ca_3(PO_4)_2$?

3. Write the simplest equation for the decomposition of phosphonium bromide, PH_4Br, by barium hydroxide, $Ba(OH)_2$ (*cf.* § 298).

4. Write the formulas of the following substances: *normal barium phosphate*, *primary ammonium phosphate*, *potassium hypophosphite*, *strontium metaphosphate*, *and silver pyrophosphate.*

5. Why is it undesirable that arsenic compounds should be used to color wall papers? Explain.

6. Show by a simple equation the reduction of arsenic trioxide by nascent hydrogen to *arsine*.

7. When a bath of Wood's metal is being melted the unmelted metal floats upon the liquid portion. Compare the specific gravity of the solid with that of the liquid. Will the liquid expand or contract on solidifying?

ELEMENT.	*Nitrogen.*	*Phosphorus.*	*Arsenic.*	*Antimony.*	*Bismuth.*
ATOMIC MASS.	14	31	75	120	207
SPECIFIC GRAVITY.	0.885 (liquid).	1.83 to 2.19	4.7 to 5.7	6.7	9.9
BOILING TEMPERATURE.	—194° C.	287°	450°	1500°	1300°
BOILING TEMPERATURE OF TRICHLORIDE.	Not known, but low.	76°	130°	223°	447°
PROPERTIES OF TRIOXIDES.	N_2O_3 is anhydride of nitrous acid.	P_2O_3 is anhydride of phosphorous acid. Weaker than nitrous acid.	As_2O_3 is both weakly acid and weakly basic.	Sb_2O_3 is like As_2O_3.	Bi_2O_3 has only *basic* properties.
PROPERTIES OF PENTOXIDES.	N_2O_5 is anhydride of nitric acid.	P_2O_5 is anhydride of phosphoric acid. Weaker than nitric acid.	As_2O_5 is anhydride of arsenic acid. Weaker than phosphoric acid.	Sb_2O_5 is anhydride of antimonic acid.	Bi_2O_5 has only *faintly* acid properties.
HYDROGEN COMPOUNDS.	NH_3 unites with HCl, HI, etc., to form salts.	PH_3 unites with acids with difficulty.	AsH_3 does not unite with acids.	SbH_3 does not unite with acids.	BiH_3 is not known to exist.

CHAPTER XX.

THE PERIODIC SYSTEM.

326. Natural Families. — During the first half of the nineteenth century various attempts were made to classify the elements. Chemists recognized the fact that there were "natural families" of elements, and that the members of the same family (called **homologous** elements), while bearing a *general* resemblance to one another, yet showed a regular *gradation* of properties in the order of the atomic masses.

We have already described two of these families, viz., the *halogen* family (*cf.* § 285) and the *nitrogen* family (*cf.* § 324).

Other natural families exist. Thus, sulphur and oxygen, with the rarer elements *selenium* (Se) and *tellurium* (Te) form a group of homologous elements. The atomic masses are, —

O, 16; S, 32; Se, 79; Te, 127.

Again, the elements *lithium*, *sodium*, and *potassium*, with the rare elements *rubidium* and *cæsium*, form the well-known "**alkali**" group of metals. The atomic masses of the three more common metals of the family are, —

Li, 7; Na, 23; K, 39.

Here, as in the case of the halogens, we find a continuous gradation of properties in the order of the atomic masses.

Lithium hydroxide, $LiOH$, is a weaker base than sodium hydroxide, $NaOH$; while potassium hydroxide, KOH, is the strongest base of the three.

327. The Periodic Arrangement. — Although the connection between the properties and the atomic masses of elements in the *same group* had been recognized for years, it was left to the Russian chemist *Mendelejeff* and the German chemist *Lothar Meyer* to discover, in 1869 to 1871, a new and peculiar relation between the properties of *all* elements and their atomic masses. This relation is the basis of the **Periodic System.**

Let us write the symbols of the first *sixteen* elements *in the order of the atomic masses.* Omitting *hydrogen*, which for the present stands almost unrelated, we have, —

Element,	Li	Gl(Be)	B	C	N	O	Fl	Na	Mg	Al
Atomic Mass,	7	9	11	12	14	16	19	23	24	27
Element,	Si	P	S	Cl	K	Ca.				
Atomic Mass,	28	31	32	35.5	39	40.				

A study of the elements from *lithium* to *fluorine*, inclusive, shows that there is a regular gradation of properties. The strongly **metallic** properties of *lithium* are weaker in *glucinum*, and yet weaker in *boron.* The *hydroxide* of boron is, in fact, called boric *acid.* In *carbon* we have an element with faintly *electro-negative*, i. e. non-metallic, properties; the elements *nitrogen* and *oxygen* are still more electro-negative; until in *fluorine* we have a **typical non-metal,** and probably the most electro-negative substance known.

The increase of atomic mass from *7* to *19* has thus continuously *diminished* the electro-positive, or metallic, character possessed by lithium, and has *increased* the electro-negative character typified by fluorine.

But after fluorine the gradation of properties does not continue; for the element *sodium*, the next greater in atomic mass, is, like lithium, one of the most typical *metals*. There is, in fact, a sudden "reversion to type"; for sodium belongs in the same natural family with lithium.

Let us, then, *proceed* in the order of atomic mass, writing the *second* set of seven elements under the first set, as in the table in § 328. *Sodium* will be under *lithium*, *magnesium* under *glucinum*, etc. We find the same gradation of properties with increase of atomic mass from *sodium* to *chlorine* as we found from *lithium* to *fluorine*.

Magnesium, like sodium, is a metal; but magnesium hydroxide is a weaker base than sodium hydroxide. *Aluminum*, the next in the order of atomic mass, is also metallic; but its hydroxide is either a base or an acid, according to circumstances. In *silicon*, the next element, metallic properties are *wanting*; silicon forms *silicic acid*. Next come *phosphorus* and *sulphur*, undoubted non-metals; and then *chlorine*, the first homologue of fluorine.

The element following chlorine is *potassium;* its atomic mass is 39. Potassium is a *typical* metal, and belongs in the same family with lithium and sodium. In passing from chlorine to potassium we have, therefore, a second instance of "reversion to type."

The properties of calcium are less metallic in character than those of potassium; for calcium hydroxide is a weaker base than potassium hydroxide. Thus, after potassium, as after sodium, variation in the properties of the elements goes on *continuously with increase of atomic mass* for another period.

From the study of "natural families" we learned that the properties of the elements in any one family vary *continuously* with the atomic mass; now we see that the properties of **all** elements, while not varying *continuously*, as in the natural family, yet vary *periodically* with the atomic mass. That is to say, a certain *increase* of atomic mass is accompanied by a *recurrence* of certain properties possessed by an element of *lower* atomic mass. The facts are summed up in what is often called the **Periodic Law,** which is, "*The properties of the elements are* **periodic** *functions of their atomic masses.*"

328. Regularities in the Periodic Arrangement. — If we write down the symbols of the elements from lithium to calcium, putting *similar* elements in the same *vertical* columns, we have an arrangement like the following: —

Li (7)	Gl or Be (9)	B (11)	C (12)	N (14)	O (16)	Fl (19)
Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)
K (39)	Ca (40)					

In this table we observe several regularities: —

(1) After every period of *seven* elements a second period of seven begins.

(2) The difference between the first and the eighth, the second and the ninth, etc., elements is in every case nearly *sixteen* units. Two successive elements of the same family are thus separated by *six* intervening elements, and differ from each other by about sixteen units of atomic mass.

(3) Elements in adjacent positions in the horizontal rows, i. e., *heterologous* elements, differ from one another by *small* numbers of units, generally only *one* or *two*. The *largest* differences occur between fluorine and sodium and between chlorine and potassium, *i. e.*, at the *break* in the periods.

329. Properties of an Element Determined. — We may call the two elements adjacent to another element in the horizontal rows the *adjacent heterologues* of the element. Thus, *boron* and *nitrogen* are the adjacent heterologues of *carbon.* The two adjacent heterologues and the two adjacent *homologues* of an element may be called the *analogues* of the element. Thus, *glucinum*, *sodium*, *calcium*, and *aluminum* are the analogues of *magnesium.*

Mendelejeff showed that if the properties of magnesium were wholly unknown they could be deduced approximately from the properties of its four *analogues.*

Thus, the *atomic mass* of magnesium (24) is very nearly the *average* of the atomic masses of its analogues.

$$\frac{9 + 40 + 23 + 27}{4} = 24.75.$$

Again, the average of the *specific gravities* of the analogues of magnesium gives approximately the specific gravity of magnes-

ium itself. The specific gravities of sodium, aluminum, glucinum, and calcium are 0.97, 2.56, 2.10, and 1.58, respectively. The average is 1.8. Experiment shows the specific gravity of magnesium to be 1.75.

Up to the time of Mendelejeff and Meyer, the existence of an element with any particular properties was regarded as an *isolated* and *accidental* fact in nature; but the periodic arrangement presents the idea that it is necessary that elements of given atomic mass shall have certain definite properties.

330. "Gaps" in the Periodic Arrangement. — When Mendelejeff first drew up his table of the elements, he found that in several cases neighboring heterologous elements did not fall *into place*, i. e., into the vertical rows containing the other members of their natural families. Thus, the element *zinc* (65) was followed by *arsenic* (75). The interval is *large*, viz., *ten* units. Now, zinc belongs in the same natural family with *magnesium;* and if arsenic follows zinc, arsenic must belong to the family of *boron* and *aluminum*. Hence the *second* and *fourth* horizontal rows would be as follows: —

2. Na (23) Mg (24) Al (27) Si (28) P (31) S (32) Cl (35.5)
4. Cu (63) Zn (65) As (75) Se (79) Br (80), etc.

This arrangement is manifestly *impossible;* for by all its properties *bromine* belongs with *chlorine*, *selenium* with *sulphur*, and *arsenic* with *phosphorus*.

The arrangement of the second and fourth rows *should* be, —

2. Na (23) Mg (24) Al (27) Si (28) P (31) S (32) Cl (35.5)
4. Cu (63) Zn (65) —— —— As (75) Se (79) Br (80).

There were, therefore, two *gaps* in the *fourth* row; a member of the *aluminum* family and a member of the *silicon* family were wanting.

331. Prediction of Unknown Elements. — Reasoning from the assumption that the properties of an element are determined by its position in the periodic grouping, Mendelejeff drew up a table stating the properties of the unknown elements that ought to exist to fill the gaps in the fourth row. The supposed element of the *aluminum* family he called **ek-aluminum,** and that of the *silicon* family, **eka-silicon.** Another gap existed in the *third* row, between *calcium* (40) and *titanium* (48). To this element Mendelejeff gave the provisional name **eka-boron.**

Mendelejeff and Meyer's tables were published in 1871. Four years afterward an element having the properties of *ek-aluminum* was discovered in France, and named **Gallium.** Its atomic mass was found to be 70, as predicted.

In 1880, Nilson and Cleve discovered in a Scandinavian mineral a new element which had the properties of *eka-boron.* They called it **Scandium.**

In 1886, Clemens Winkler discovered the element which he called **Germanium.** Upon comparing the properties of this element (its atomic mass is 72) with those foretold for eka-silicon, he decided that the new element could be nothing else than the eka-silicon predicted by Mendelejeff fifteen years before.

332. The Table of the Elements.—The periodic system of the elements is given on the following page. The student will notice that there are *eight* instead of *seven* groups. This is due to the fact that there are three groups of three elements each that do not fit into the table of seven. The first of these groups consists of the elements *iron*, *cobalt*, and *nickel*, whose atomic masses place them between *manganese* (55) and *copper* (63). These three groups of elements constitute Group VIII.

The valence of the elements of Group IV in their highest *hydrogen* compounds is 4; from Group IV to Group VII the valence toward hydrogen *decreases*.

The valence of the elements in their highest *oxygen* compounds *increases* from Group I to Group VII.

M is the *general symbol* of all the elements.

333. Conclusion.—Besides resulting in the *prediction* of the properties of undiscovered elements, the periodic classification has led to a more careful study of the atomic masses of *known* elements.

The classification has many *faults*, but it is full of suggestions, and shows a *striking* relationship between the elements. Because of this relationship chemists are tending to the belief that all the elements are modifications of some yet simpler forms or form of matter. As to the character of this fundamental substance, nothing is known at present. A recent irregularity in the periodic arrangement results from the fact that the atomic mass of tellurium has been placed at about 127, or slightly higher than iodine, 126.9. This is not startling, however, for the periodic recurrence of properties is only *approximate*, at the best.

The Periodic Table.

GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
—	—	—	MH_4	MH_3	MH_2	MH	
M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	
H 1							
Li 7	Be 9	B 11	C 12	N 14	O 16	Fl 19	
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5	
K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56, Co 59, Ni 59.
Cu 63.6	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80	
Rb 85	Sr 87.6	Y 89	Zr 90.6	Nb 94	Mo 96	—	Ru 102, Rh 103, Pd 106.
Ag.108	Cd 112	In 114	Sn 119	Sb 120	Te,127.5	I 126.9	
Cs 133	Ba 137	La 138	Ce, 140	{ Pr 140 } { Nd 144 }	—	Sa 150	— — —
—	—	—	—	—	—	—	
—	—	Yb 173	—	Ta 183	W, 184	—	Os 191, Ir 193, Pt 195.
Au 197	Hg,200	Tl 204	Pb,207	Bi 208	—	—	
—	—	—	Th 232	—	U, 239	—	

334. The Argon Family. — The discovery of argon and the elements related to it, viz., *helium*, *neon*, *krypton*, and *xenon*, has led to the introduction of a new family into Chemistry, — the Argon family (*cf.* § 115). Ramsay suggests (November, 1900) that the group may be placed in a vertical row at the left of the alkali group in the table. These two vertical rows would then look something like this: —

He 4	Li 7
Ne 20	Na 23
Ar 40	K 39
	Cu 63
Kr 82	Rb 85.4
	Ag 108
Xe 128	Cs 133

The fact that argon (40) comes before potassium (39) need cause no more anxiety than the fact that tellurium (127.5) precedes iodine (126.9). The properties of the elements are only *approximately*, not *absolutely*, periodic functions of the atomic masses.

The elements of the argon group are all *monatomic*; and their *valence* is, apparently, *o*.

CHAPTER XXI.

SILICON AND BORON.

A. Silicon.

335. **Occurrence of Silicon.** — As was stated in § 6, silicon is, next to oxygen, the most abundant constituent of the earth's crust. It is not found free, but in the form of its oxide, SiO_2, and in *silicates*, i. e., the salts of *silicic acid*. Silicon dioxide (silica) and the silicates make up sand, clay, and almost all the crystalline rocks of the earth's crust.

Silica is taken up by plants. The *straw* and *husks* of the grains contain it. The *equisetum* is called "scouring-rush," from the large amount of silica present in it. Silica is found, also, in the skin, nails, hair, etc., of animals.

Certain microscopic plants, the **diatoms**, have skeletons of silica; and these have accumulated in large deposits in some places.

336. **Preparation.** — Silicon, like carbon, exists in several *allotropic* forms. The **amorphous** variety may be obtained by heating a mixture of powdered *quartz* and powdered *magnesium*.

$$2\ Mg + SiO_2 \longrightarrow 2\ MgO + Si.$$

Amorphous silicon is a brown powder which burns, when heated in the air, to silicon dioxide. It is attacked by *hydrofluoric acid*, but not by other acids.

$$Si + 4\ HFl \longrightarrow SiFl_4 + 2\ H_2.$$

Silicon is obtained **crystalline** by heating *sodium fluosilicate*, Na_2SiF_6, with sodium and zinc.

$$Na_2SiF_6 + 4\ Na \longrightarrow 6\ NaFl + Si.$$

The silicon dissolves in the melted zinc, and separates out in crystals as the zinc cools. When the zinc solidifies it encloses the silicon. The zinc is then removed by treating the mass with hydrochloric acid; and silicon remains.

The crystalline form of silicon does not burn in air or oxygen, nor does it dissolve in acids. It dissolves in hot sodium hydroxide solution, giving *sodium silicate* and hydrogen. The simplest equation is, —

$$Si + 4\ NaOH \longrightarrow Na_4SiO_4 + 2\ H_2.$$

337. **Silicon Compounds.** — The general structure of silicon compounds is like that of the corresponding carbon compounds. *Hydrogen silicide*, SiH_4, corresponds to *marsh gas*, CH_4; *silicon tetrachloride*, $SiCl_4$, to *carbon tetrachloride*, CCl_4; *silicon dioxide*, SiO_2, to *carbon dioxide*, CO_2; *silicic chloroform*, $SiHCl_3$, to *chloroform*, $CHCl_3$.

Hydrogen silicide is a colorless gas. It may be obtained, mixed with hydrogen, by treating *magnesium silicide* with dilute hydrochloric acid.

$$Mg_2Si + 4\ HCl \longrightarrow SiH_4 + 2\ MgCl_2.$$

As ordinarily made, it ignites *spontaneously* in the air.

$$SiH_4 + 2\ O_2 \longrightarrow SiO_2 + 2\ H_2O.$$

Magnesium silicide is prepared by heating powdered quartz with an *excess* of magnesium powder.

$$4\ Mg + SiO_2 \longrightarrow Mg_2Si + 2\ MgO.$$

If too little magnesium is used, amorphous silicon results (*cf.* § 336).

Silicon tetrachloride is a colorless liquid, boiling at 59° C. It is formed from silicon and chlorine. Water decomposes it, giving *silicic acid* and *hydrochloric acid.*

$$SiCl_4 + 4\ H_2O \longrightarrow Si(OH)_4 + 4\ HCl.$$

(*Cf.* the action of *phosphorus trichloride* with water, § 303.)

Silicon tetrafluoride is a colorless gas, formed when silicon dioxide is treated with hydrofluoric acid.

$$SiO_2 + 4\ HFl \longrightarrow SiFl_4 + 2\ H_2O.$$

Silicon tetrafluoride is decomposed by water as the *tetrachloride* is.

$$SiFl_4 + 4\ H_2O \longrightarrow Si(OH)_4 + 4\ HFl.$$

Instead of being set free, however, the hydrofluoric acid unites with some of the silicon tetrafluoride, forming **fluosilicic acid,** H_2SiFl_6. The name "fluosilicic acid" means *silicic* acid, H_2SiO_3, with its *oxygen* replaced by fluorine, — *three* bivalent oxygen atoms by *six* univalent fluorine atoms (*cf.* § 314, *sulpharsenites*, and § 194, *thiosulphates*). Many *fluosilicates* are known; **potassium fluosilicate,** K_2SiFl_6, is one of the few difficultly soluble potassium salts.

338. Silicon Carbide. — Silicon carbide (SiC) or **carborundum** is among the three hardest substances known, the others being *boron carbide* and the diamond. It is made by heating a mixture of powdered quartz, coke, saw-dust, and common salt in the electric furnace.

Carborundum is not attacked by acids nor by solutions of alkalies. It burns only with great difficulty. Because of its hardness, powdered carborundum is used as a polishing and cutting agent.

339. Silicon Dioxide. — Silicon dioxide is found as sand, quartz, etc. (*cf.* § 335). The pure substance may be prepared by heating silicic acids, H_4SiO_4, H_2SiO_3, etc.

$$H_4SiO_4 = SiO_2 + 2\ H_2O.$$
$$H_2SiO_3 = SiO_2 + H_2O.$$

Silicon dioxide is thus *silicic anhydride.*

When any form of silicon dioxide is fused with sodium or potassium hydroxide or carbonate, sodium or potassium *silicate* results.

$$2\ NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O.$$
$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2.$$

Calcium carbonate acts in the same way.

When silica is fused with the *oxide* of a metal, a silicate is also formed.

$$CaO + SiO_2 = CaSiO_3.$$

Acids do not act upon silica (except hydrofluoric acid as in § 337).

340. Silicic Acid. — When a soluble silicate is treated with hydrochloric acid, a bulky mass, like gelatine, is precipitated. This probably consists of *normal* silicic acid, H_4SiO_4. When the gelatinous mass is dried at the ordinary temperature, it loses water and becomes a non-crystalline powder. This is probably *ordinary* silicic acid, H_2SiO_3. When the powder is heated to a *high* temperature it loses water, forming silica, SiO_2. The equations are given in § 339.

Polysilicic Acids. — Besides the normal and ordinary forms of silicic acid, many other forms are possible; these are known as **polysilicic** acids. They are derived from normal silicic acid by the loss of different proportions of water. A general formula for them all would be, —

$$x\ \mathrm{Si(OH)_4} - y\ \mathrm{H_2O}.$$

Thus, if $x = 2$ and $y = 1$, we have, —

$$2\ \mathrm{H_4SiO_4} - \mathrm{H_2O} = \mathrm{H_6Si_2O_7}.$$

Among the varieties of *amorphous* silica found in nature are *agate*, *chalcedony*, *opal*, *carnelian*, *flint*, *amethyst*, etc. These all contain *water*, and may therefore be looked upon as forms of the polysilicic acids. The colors of these substances are usually due to traces of impurities.

341. Silicates. — The silicates are salts of silicic acid. The mineral *chrysolite* is *magnesium silicate*, Mg_2SiO_4. *Serpentine* is $Mg_3Si_2O_7$. These are salts of the acids H_4SiO_4 and $H_6Si_2O_7$, respectively. *Potassium*, *sodium*, and *calcium silicates* are derived from the acid H_2SiO_3.

Potassium silicate is known as "water glass"; it is used to make cements and artificial stone. **Kaolin** is practically pure aluminum silicate, $Al_2(SiO_3)_3$. It fuses only at a very *high* temperature. It is used for making china and crockery ware, fire-bricks, etc. **Clay**, which is *impure* aluminum silicate, melts lower than kaolin; it is used for making pottery, bricks, etc. The red color of baked clay is due to *ferric silicate*, $Fe_2(SiO_3)_3$.

342. Glass. — Glass is a mixture of certain *silicates*, generally of sodium or potassium silicate with calcium or lead silicate.

The silicates of calcium, lead, etc., *crystallize* when they solidify: a glass made from them would break into fragments on cooling. The silicates of sodium and potassium, however, not only do not crystallize themselves, but even *prevent the other silicates from crystallizing.*

Ordinary, soft glass, such as is used for window panes and bottles, is essentially a mixture of the silicates of *calcium* and *sodium;* it may be made by melting together *silica, calcium carbonate,* and *sodium carbonate,* in the proper proportions.

Hard glass is a mixture of the silicates of *calcium* and *potassium.* It is used for making chemical apparatus, lamp globes, etc.

Flint glass, such as is used in making optical instruments, etc., is a mixture of *potassium and lead silicates.*

Enameled or "**milky**" glass is made by adding *cryolite* (*cf.* § 266) to ordinary glass.

"**Granite ironware**" or "*porcelain-lined*" *ware* consists of iron covered with an easily fusible glass, called *enamel.*

Color is imparted to glass by the addition of small amounts of other substances. Thus, a *cobalt* compound colors glass *blue ;* a *cuprous* compound, *red ;* a *chromic* compound, *green.*

The **etching** of designs on glass is done with *hydrofluoric acid*, as described in § 268. In certain kinds of etching a blast of sand is used.

Pressed glassware is made in molds ; in **cut** glassware the designs are ground or polished by means of *emery*, *carborundum*, or *sandstone* wheels.

All articles of glass, to be permanent, must be **annealed.** Annealing consists in allowing the hot object to cool *regularly*, so that its molecules may assume *permanent* positions with reference to one another. Unannealed glass may fly to pieces at the slightest jar.

B. Boron.

343. Occurrence of Boron. — The element *boron* is the first member of the aluminum group of elements (*cf.* page 313); yet in its free state it closely resembles silicon and carbon. It occurs in nature chiefly as *boric acid* (H_3BO_3) and as *borax* ($Na_2B_4O_7$).

Boric acid is found chiefly in Tuscany, where it issues, mixed with steam, from the earth. Borax is found in Nevada and California in dried borax lakes. *Boracite*, $(Mg_3B_8O_{15})_2 \cdot MgCl_2$, occurs at Stassfurt, in Germany.

344. Preparation. — Boron exists in *two* allotropic forms, — the *amorphous* and the *crystalline ;* it is difficult to prepare either form in a pure state.

Crystalline boron is made by heating boron trioxide, B_2O_3, with aluminum. The aluminum reduces the oxide ; and the liberated boron dissolves in the excess of aluminum. When the cooled mass is treated with hydrochloric acid, the aluminum dissolves, leaving crystals of boron.

345. Properties. — Crystalline boron has a specific gravity of 2.6, and resembles the diamond. The *amorphous* form is brown. It *burns* when heated in the air, giving *boron trioxide*, B_2O_3. Nitric acid converts it into boric acid. The crystalline form is more difficult to ignite than the amorphous.

Boron dissolves in melted sodium hydroxide, giving sodium borate. When it is heated in nitrogen or ammonia it gives *boron nitride*, BN. This is a white powder which is decomposed by steam, giving *boric acid* and *ammonia.*

$$BN + 3\ H_2O \longrightarrow B(OH)_3 + NH_3.$$

With chlorine, boron forms *boron trichloride*, BCl_3, a colorless liquid. This is decomposed by water, giving boric acid and hydrochloric acid (*cf.* §§ 303 and 337).

$$BCl_3 + 3\ H_2O \longrightarrow B(OH)_3 + 3\ HCl.$$

346. Boric Acid. — Boric acid is made by adding concentrated hydrochloric or nitric acid to a hot solution of borax. It is a white, crystalline solid. Its aqueous solution has a faintly acid reaction with litmus, but colors *turmeric* paper *brown*, just as sodium hydroxide does. Boric acid is in some respects like *aluminum hydroxide*, which is an acid or a base, according to circumstances.

Boric acid is *volatile with steam*, as was indicated in § 343. Its solution in ethyl alcohol burns with a bright green flame. When boric acid is heated it loses water, giving finally the *anhydride*, B_2O_3. This redissolves readily in water, giving the acid.

347. Borax. — The ordinary *borates* are derived not from the *normal* acid, H_3BO_3, but from *tetraboric* acid, $H_2B_4O_7$. This is related to the normal acid just as the *polysilicic acids* are to normal silicic acid (*cf.* § 340).

$$4\ H_3BO_3 - 5\ H_2O = H_2B_4O_7.$$

Borax is **sodium tetraborate**, $Na_2B_4O_7$. It comes into the market as crystals which are either $Na_2B_4O_7.10\ H_2O$ or $Na_2B_4O_7.5\ H_2O$.

When heated, borax loses its crystal-water and swells to a porous mass; on stronger heating, this melts to a clear glass. Molten borax dissolves the oxides of metals, and with some of them gives characteristic colors; hence its use in the *laboratory* to form the "borax bead," and in the *arts* to clean the surfaces of metals before *soldering* and *welding*, and before coating metals with enamel (*cf.* § 342).

Borax is used, also, to prevent the decomposition of organic substances, in medicine, in the manufacture of hard-water soaps, and to increase the gloss of starch.

348. Exercises.

1. Name some of the scouring mixtures which consist essentially of silica.
2. Suggest a *possible* reason for the fact that silicon dioxide is a hard, infusible solid, while the corresponding oxide of carbon is gaseous.

[illegible] a [illegible]
[illegible] in [illegible]
be [illegible]

[illegible] ust be [illegible]
[illegible] in [illegible]
[illegible] *ate* is [illegible]
[illegible] word [illegible]
[illegible] the rela[illegible]

[illegible] ons, *by* [illegible]
[illegible] senting the [illegible]

CHAPTER XXII.

DISSOCIATION AND MASS ACTION.

349. Dissociation by Heat. — We have already learned of several cases of dissociation by heat, *e. g.*, the decomposition of *steam* (*cf.* § 45) and of *hydriodic acid* (*cf.* § 276). The essential things in a dissociation are the constant *decomposition of complex molecules* into simpler ones, and the constant *recombination* of the simpler molecules, until a definite equilibrium is established.

The dissociation of iodine (*cf.* § 274) is recognized by the fact that while *below* 600° C. the molecular mass of iodine vapor is 254, *above* this temperature the molecular mass *diminishes*, until at about 1500° C. it becomes practically 127. This diminution of the molecular mass means that the *number* of molecules has *increased.* I_2 molecules have become *monatomic* (I).

350. Dissociation in Solution; Ionization. — Dissociation takes place not only at elevated temperatures, but, *in many cases*, in solution. It is recognized just as heat-dissociation is, viz., by *an increase in the number of molecules.* As we have already learned (*cf.* §§ 244 and 245), the molecular mass of a *soluble* substance can be obtained from the osmotic pressure, and from the freezing-point and the boiling-point of the solution. When, however, we come to apply these methods to a substance like *sodium chloride*, we notice that the molecular mass is too *small*, and in dilute solution only about *one-half* of what we should expect.

To illustrate: An aqueous solution of *cane-sugar* ($C_{12}H_{22}O_{11}$) containing 342 grams of sugar to the liter (342 is the molecular mass of cane-sugar) freezes at about —1.8° C.; so does a solution of *grape-sugar* ($C_6H_{12}O_6$), containing 180 grams of sugar to the liter. But the freezing-point of a solution of *sodium chloride* containing 58.5 grams of salt to the liter approaches —3.6° C.; the depression is thus *twice* as great as we should expect. This can be due only to the presence of *twice as many molecules* as we should expect: the molecules of sodium chloride must have *dissociated* in aqueous solution.

Many other substances, e. g., ***hydrochloric acid***, ***nitric acid***, *potassium* and ***sodium hydroxides***, ***potassium chloride***, *sodium nitrate*, etc., are like sodium chloride. The depression of the freezing-point, the elevation of the boiling-point, and the osmotic pressure of aqueous solutions of these substances all show that the number of molecules present in solution is greater than we should expect — in *dilute* solution practically *twice* as great. The molecules of *sodium sulphate*, *sulphuric acid*, etc., dissociate into *three* particles in dilute solution.

The **electric conductivity** of solutions supports the theory of dissociation; for the electric current can pass readily only through solutions containing substances whose molecules dissociate in solution. Pure water has a conductivity that is almost *nil;* the conductivity of sugar solution is also *very small;* but aqueous solutions of ***strong acids***, ***strong bases***, and the ***salts*** formed from them ***conduct readily***. The substances just named are, therefore, called **electrolytes,** and dissociation in solution is called **electrolytic** dissociation. The particles into which an electrolyte dissociates are called **ions**; hence the dissociation is called, also, **ionization.**

Composition of a Solution. — A solution of sodium chloride in water is, then, not merely a mixture of the molecules of these two substances. In the first place, most of the sodium chloride molecules are dissociated into sodium and chlorine *ions*. Since *recombination* goes on at the same time, the behavior of sodium chloride in water is shown by the *equilibrium* equation (*cf.* § 276), —

$$NaCl \rightleftarrows \overset{+}{Na} + \overset{-}{Cl}.$$

But the water, too, is dissociated *slightly*, —

$$H_2O \rightleftarrows \overset{+}{H} + \overset{-}{OH}.$$

Hence combination may take place between *sodium* and *hydroxyl* ions and between *hydrogen* and *chlorine* ions to form undissociated ***sodium hydroxide*** and *hydrochloric acid*, respectively. We have, therefore, present in an aqueous solution of sodium chloride ***eight*** distinct things: the *ions* hydrogen, hydroxyl, sodium, and chlorine, and the *undissociated* substances water, sodium chloride, sodium hydroxide, and hydrochloric acid.

351. Explanation of Neutralization. — A very simple explanation of the properties of acids, bases, and salts, and of ***neutralization*** follows from the ionization theory. All ***acids*** in aqueous solution affect litmus in the same way because they all give *hydrogen ions*. The turning of litmus *red* is simply an indication of the presence of these ions. Similarly, *bases* are substances whose solutions contain hydroxyl $(\overset{-}{O}H)$ ions.

Neutralization is thus essentially the union of hydrogen and hydroxyl ions to form undissociated molecules of water.

This new definition of neutralization is supported by the fact that the amount of *heat* evolved when the several strong acids are neutralized by a given base is approximately the same *if equal numbers of molecules of the acids are taken.* Thus, *63* grams of nitric acid, *36.5* grams of hydrochloric acid, and *49* grams of sulphuric acid all liberate practically the same quantity of heat when neutralized by sodium hydroxide. Sulphuric acid has the molecular mass *98;* but its molecule gives *two* hydrogen ions; hence 49 grams of sulphuric acid are equivalent to 63 grams of nitric acid and to 36.5 grams of hydrochloric acid.

The *ionic equation* for the neutralization of sodium hydroxide by hydrochloric acid is, —

$$\overset{+}{Na} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{Cl} \longrightarrow \overset{+}{Na} + \overset{-}{Cl} + H_2O.$$

When we evaporate the water we get union of the sodium and chlorine ions; and *sodium chloride* is formed.

352. "Test" Reactions are Ionic. — What we call *tests* for classes of substances, *e. g.*, the action of *silver nitrate* solution with *chlorides*, and of *barium chloride* solution with *sulphates*, are really tests for *free ions.* Thus, when we add silver nitrate solution to a solution of sodium chloride, the equation is, —

$$\overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{NO_3}} + \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}} \longrightarrow \mathit{AgCl} + \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{NO_3}}.$$

The *silver chloride*, being practically *insoluble*, is almost all removed as a precipitate.

If, however, we add silver nitrate solution to a dilute solution of *sodium chlorate*, $NaClO_3$, we do not get a precipitate of silver chloride, *because no chlorine ions are present.* The chlorine of sodium chlorate is part of the ion $\overline{Cl}O_3$. *Silver chlorate*, which might be formed, is not precipitated because soluble. Hence *no result is apparent.*

$$\overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{NO_3}} + \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{ClO_3}} \longrightarrow \overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{NO_3}} + \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{ClO_3}}.$$

Another illustration: *Ferrous chloride*, $FeCl_2$, gives with *ammonium sulphide*, $(NH_4)_2S$, a black precipitate of *ferrous sulphide*, FeS; but ammonium sulphide does *not* precipitate the iron of *potassium ferrocyanide* solution, $K_4Fe(CN)_6$, *because iron ions are not present.*

$$\mathrm{K_4Fe(CN)_6} \longrightarrow 4\,\overset{+}{\mathrm{K}} + \overset{-}{\mathrm{Fe(CN)_6}}.$$

353. Electrolysis. — What we call *electrolysis* is not the tearing apart of molecules by the electric current, but the *carrying* of electric charges by the *ions* from one electrode to the other. When we *electrolyze* dilute sulphuric acid, as in § 37, we have, *before the introduction of the electrodes into the acid*, ionization of most of the sulphuric acid molecules.

$$\mathrm{H_2SO_4} \longrightarrow 2\,\overset{+}{\mathrm{H}} + \overset{-}{\mathrm{SO_4}}.$$

The current passes because the hydrogen ions carry + charges from the + to the — electrode, and the *sulphuryl* (SO_4) ions — charges from the — to the + electrode. The bivalent SO_4 ion can carry as great a charge as *two* univalent hydrogen ions.

The charged ions ($\overset{+}{H}$ and $\overset{-}{SO_4}$) are **not atoms**; neither have they all the properties of free molecules. When they reach their respective electrodes, however, they take on their ordinary properties. The *hydrogen* ions give up their + charges at the — electrode, and become neutral *atoms*. These unite to form hydrogen *molecules*. The *sulphuryl* ion gives up its — charge at the + electrode, and becomes the **radical** SO_4. This, being unstable, acts upon water, giving *sulphuric acid* and *atomic oxygen*.

$$SO_4 + H_2O \longrightarrow H_2SO_4 + \text{—}O\text{—}.$$

The oxygen atoms unite to give *molecules* of oxygen (O_2) or of *ozone* (O_3; *cf.* § 287).

354. Hydrolysis. — While *strong* acids, like *hydrochloric acid*, etc., are much dissociated in solution, *weak* acids, like *carbonic acid*, *hydrocyanic acid*, etc., are dissociated only slightly. Consequently, when we dissolve the salt formed from a *weak* acid and a *strong* base, *e. g.*, *sodium carbonate*, we get the reaction of the base, *i. e.*, of *OH ions*.

That this must be so is seen from the equation,

$$2\,\overset{+}{Na} + \overset{-}{CO_3} + 2\,\overset{+}{H} + 2\,\overset{-}{OH} \longrightarrow H_2CO_3 + 2\,\overset{+}{Na} + 2\,\overset{-}{OH}.$$

The carbonic acid is only *slightly* dissociated; hence relatively few *hydrogen* ions remain in the solution, while the *hydroxyl* ions are present in excess. Therefore sodium carbonate solution reacts **alkaline.**

The dissociation of the salts formed by *weak bases* and *strong acids* is similar; only in this case we get the reaction of the *acid*, i. e., of *hydrogen ions.*

Thus, when ferric chloride is dissolved in water, the ionic equation is, —

$$\overset{+}{Fe} + 3\,\overset{-}{Cl} + 3\,\overset{+}{H} + 3\,\overset{-}{OH} \longrightarrow Fe(OH)_3 + 3\,\overset{+}{H} + 3\,\overset{-}{Cl}.$$

Here the *ferric hydroxide*, $Fe(OH)_3$, being a weak base and little dissociated, removes many *OH* ions from the "sphere of action"; hence the *H* ions determine the reaction of the solution.

Ferric chloride solution reacts acid. Morever, its *rusty* color shows that much undissociated ferric hydroxide (iron rust) is present in it.

The illustrations just given are cases of **hydrolysis,** *i. e.*, of "decomposition by water."

355. Mass Action. — The recombination of dissociated particles, whether in gaseous form or in solution, is influenced by the *frequency* with which the particles *meet.* If, therefore, we wish to *stop* or to *diminish* the dissociation of a substance *AB*, we simply see to it that a *large excess* of one of the dissociated particles, *e. g.*, *A*, is present. The **active mass** of *A*, that is, the mass of it that can combine with *B*, is thus increased.

The effects due to an **excess** of dissociated particles are cases of **Mass Action.**

To illustrate: When we attempt to get the molecular mass of *phosphorus pentachloride*, PCl_5, by vapor density methods, we find that the molecular mass is too *low*, owing to the dissociation of some of the molecules into *phosphorus trichloride* and *chlorine*.

$$\mathrm{PCl_5} \rightleftarrows \mathrm{PCl_3} + \mathrm{Cl_2}.$$

The dissociation can be prevented if the vapor density determination is carried out in an atmosphere of phosphorus trichloride; because the chlorine molecules then meet molecules of phosphorus trichloride so frequently that practically no chlorine molecules remain free.

Similar effects occur in solution. Thus, if we wish to precipitate the sulphuric acid, *i. e.*, the *SO_4 ions*, contained in a solution, we use *barium chloride* solution. If we use exactly the *theoretical* amount of barium chloride, however, much barium sulphate remains in solution (as *Ba* and *SO_4* ions). The reaction is only partly represented by the equation,

$$\overset{+}{\mathrm{Ba}} + 2\,\overset{-}{\mathrm{Cl}} + 2\,\overset{+}{\mathrm{H}} + \overset{-}{\mathrm{SO_4}} \longrightarrow \mathrm{BaSO_4} + 2\,\overset{+}{\mathrm{H}} + 2\,\overset{-}{\mathrm{Cl}},$$

for the *reverse* operation also goes on.

$$\mathrm{BaSO_4} \longrightarrow \overset{+}{\mathrm{Ba}} + \overset{-}{\mathrm{SO_4}}.$$

Whatever will cause the *SO_4* ions to meet more *Ba* ions in a given time will increase the precipitation of the *SO_4* ions as barium sulphate. We obtain this result by adding a large *excess* of barium chloride solution.

356. Exercises.

1. What substances are present in a solution of potassium nitrate in water? Why is the reaction neutral?

2. Make a definition of an acid in terms of the ionization theory. Of a salt.

3. The reaction of a solution of *potassium cyanide*, KCN, is *alkaline ;* so is that of a solution of *disodium hydrogen phosphate*, Na_2HPO_4. Explain.

4. Write the *ionic* equation for the neutralization of *hydrobromic acid*, HBr, by *potassium hydroxide.* Explain.

5. Cold, *concentrated* sulphuric acid does not act upon zinc, but the *dilute* acid does. Explain.

6. Explain, in terms of the ionic theory, the action of *hydrogen sulphide*, H_2S, upon *cupric sulphate* solution (*cf.* § 182).

7. To precipitate all the *manganese* of a manganese sulphate solution as *sulphide* (*cf.* § 182), we use a decided *excess of ammonium sulphide*, $(NH_4)_2S$. Why?

CHAPTER XXIII.

METALS.

357. Metals and Non-Metals. — In our previous work we have studied chiefly *non-metallic* elements. There is, however, no sharp distinction between metals and non-metals, but rather a gradual change from one class to the other (*cf.* § 327). But just as *oxygen*, *chlorine*, and *sulphur* have a *distinct* character, which no one would mistake for that of a metal, so there are certain elements having a *typical* metallic nature.

Metals are usually opaque, and their polished surfaces are good reflectors of light; hence the **metallic luster.** They are good conductors of heat and electricity. With oxygen and hydrogen the metals form *bases;* and by replacing the hydrogen of acids, i. e., *ionic* hydrogen, they form *salts.*

Some elements, e. g., *antimony*, are both **acid-forming** and base-forming; they are often called **metalloids.**

358. Occurrence of Metals. — The solid elements and compounds found in nature are called **minerals.** The minerals and mixtures of minerals from which metals are obtained are called **ores.** Some metals, e. g., *gold* and *copper*, occur *free*, that is, *uncombined* with other elements; but most metals are found as *oxides* or *sulphides.* Some metals are found as *carbonates, hydroxides*, etc.

359. Extraction of Metals from Their Ores. — If metals occur **free** they may be separated by mechanical means from minerals mixed with them. An illustration is the crushing of an ore in a stamp-mill and the washing away of the lighter materials. *Copper* and *gold* are extracted in this way, although *chemical* methods are employed with inferior ōres of these metals.

The most **common** method of extracting metals is to reduce the **oxide** with carbon (charcoal or coke). This is the case with iron. If the ores used are not oxides, they are usually converted into oxides by "roasting" (*cf.* § 178). *Sulphides, hydroxides*, and *carbonates* may thus be changed into *oxides.*

Another method of rēducing an oxide is to heat it in a stream of *hydrogen.* The oxygen and hydrogen unite and escape as *steam*, while the metal is left. This is a good *laboratory* method; but it is too expensive for commercial use.

Chlorides are sometimes reduced by heating them with *sodium. Aluminum* was *formerly* obtained in this way from its chloride.

Several of the metals, e. g., *aluminum*, are obtained by the action of the **electric current** upon some of their compounds.

360. Properties of the Metals. — Besides the *general* properties already mentioned, the metals possess other properties in varying degrees. Thus, some metals, e. g., *sodium* and *lead*, are soft; while others, e. g., *chromium* and *manganese*, are hard. ***Sodium*** and ***lithium*** are light enough to float on water, while gold is *19.3* and platinum *21.5* times as heavy as water.

Again, some metals evolve much energy in uniting with oxygen, while others form very *unstable* oxides. Usually the *lighter* metals, such as sodium and potassium, are very active chemically, and form *strong* bases; while the *heavy* metals, such as lead and gold, are much less active.

CHAPTER XXIV.

THE ALKALI METALS.

361. General Properties. — The metals, like the non-metals, are generally studied in groups or natural families based upon similarity of properties. The **Alkali** group consists of the *five* metals named below and the *radical* ammonium, NH_4, the compounds of which resemble those of sodium and potassium (*cf.* § 148). These metals are called "alkali" metals because the two most important members of the group are contained in the *alkalies*, i. e., in sodium and potassium hydroxides.

ELEMENT.	SYMBOL.	ATOMIC MASS.	SPECIFIC GRAVITY.	MELTING POINT.
Lithium.	Li	7	0.59	180° C.
Sodium.	Na	23	0.97	95.6° C.
Potassium.	K	39	0.87	62.5° C.
Rubidium.	Rb	85.4	1.52	38.5° C.
Cæsium.	Cs	133	1.85	26.5° C.

All of these metals have a silvery white luster and are easily cut. In air they become coated with a layer of the *oxide* and the *hydroxide;* if *carbon dioxide* is present, these pass into the corresponding *carbonates.* The alkali metals burn when heated in air, and decompose water at ordinary temperatures; therefore none of them is found *free* in nature. The salts of these metals are practically all soluble in water.

The properties of the alkali metals change in the order of the atomic masses, *e. g.*, the higher the atomic mass the lower the melting-point. The chemical activity and the electro-positive character *increase* from *lithium* to *cæsium.* Cæsium is the most electro-positive element known.

362. **Lithium.** — Lithium is widely distributed in nature, but no mineral known contains a large proportion of it. It is found in *minute* quantities in most mineral waters, in many plants, and in the blood. Lithium is the lightest of the metals. Its salts color the Bunsen flame *crimson.*

363. **Sodium.** — Sodium occurs widely distributed and in large quantities, especially as *sodium chloride,* NaCl. This exists as *rock-salt* and *sea-salt,* and in many mineral springs. *Sodium silicate* is found in many rocks; the *nitrate* is Chili saltpeter. Large deposits of the sulphate and carbonate exist. The ashes of plants growing in or near the sea contain sodium carbonate, and were formerly the source of many sodium compounds.

364. Preparation and Properties of Sodium. — At present, sodium is prepared by the *electrolysis* of sodium hydroxide, or of *sodium chloride*. Strontium chloride or potassium chloride is added to the sodium chloride to lower the melting-point.

Formerly the metal was made by heating a mixture of the carbonate and charcoal in the absence of air.

$$Na_2CO_3 + 2\,C \longrightarrow 2\,Na + 3\,CO.$$

The sodium which distilled off was first condensed to a liquid, and was then collected under petroleum.

Sodium is a white, soft metal that can be moulded between the fingers, and can be readily pressed into wire. Although so soft at ordinary temperatures, it is quite *hard* at —20° C. It decomposes water, producing sodium hydroxide and hydrogen (*cf.* § 46); this method is used to prepare *pure* sodium hydroxide.

Sodium unites readily with oxygen (*cf.* § 289), producing a mixture of the *monoxide* (Na_2O) and the *peroxide* (Na_2O_2). The properties of the pure *monoxide* are not known. The *peroxide* has recently come into general use as an oxidizing and bleaching agent and as a source of free oxygen. It is decomposed by water, giving, finally, *sodium hydroxide* and *oxygen*.

$$(1)\ Na_2O_2 + 2\,H_2O \longrightarrow 2\,NaOH + H_2O_2.$$
$$(2)\ 2\,H_2O_2 = 2\,H_2O + O_2.$$

An alloy of *sodium* and *mercury*, called **sodium amalgam**, is a useful reducing agent; it is simply *diluted* *sodium.* An amalgam is an *alloy* of which *mercury* is one constituent.

365. Sodium Hydroxide. — Sodium hydroxide, or *caustic soda*, is formed when sodium or either of its oxides acts upon water. Two of the *commercial* methods of preparing the hydroxide are as follows: —

(1) Boiling a solution of *sodium carbonate* with *slaked lime* (calcium hydroxide).

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2\ NaOH + CaCO_3.$$

The calcium carbonate, being insoluble, is precipitated. The sodium hydroxide solution is drawn off and evaporated.

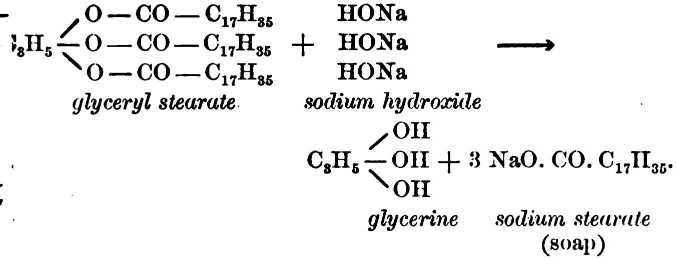
(2) Electrolysis of a concentrated solution of *sodium chloride.*

$$2\ NaCl + 2\ H_2O \longrightarrow 2\ NaOH + H_2 + Cl_2.$$

The sodium hydroxide and hydrogen collect at the — electrode.

Sodium hydroxide is a white, deliquescent solid, very soluble in water. Both the solid and its solution absorb carbon dioxide readily. The solution has a *soapy* feeling, and turns red litmus blue.

366. Soap. — Sodium hydroxide is one of the strongest and most useful bases. When fats are boiled with it they are *saponified*, i. e., converted into soap. The fats are chiefly *glyceryl salts of organic acids.* They are decomposed by sodium hydroxide into *glycerine* and the organic acid. The sodium salt of the organic acid is *soap.*



$$C_3H_5\begin{cases}O-CO-C_{17}H_{35}\\O-CO-C_{17}H_{35}\\O-CO-C_{17}H_{35}\end{cases}+\begin{array}{c}HONa\\HONa\\HONa\end{array}\longrightarrow C_3H_5\begin{cases}OH\\OH\\OH\end{cases}+3\,NaO.CO.C_{17}H_{35}.$$

glyceryl stearate *sodium hydroxide* *glycerine* *sodium stearate* (soap)

The sodium stearate formed is "salted out" of solution by adding sodium chloride.

When soap is dissolved in water it is partly *hydrolyzed* (*cf.* 354) into sodium hydroxide and the organic acid; the sodium hydroxide is the cleansing agent. When soap is put into *hard* water, an insoluble scum is formed; this is the *calcium* salt of the organic acid.

367. Sodium Carbonate. – Sodium carbonate, or *soda*, is one of the most important chemicals manufactured. The principal methods of making it are the **Solvay**, or *Ammonia*, **Process** and the **Le Blanc Process.** The second of these is the more interesting *historically*, because it was devised by Le Blanc for the French government during the Revolution, when the supply was cut off; but the ammonia process is so much cheaper that fully three-fourths of the soda used is now made in this way. Both processes begin with common salt.

The **Solvay Process** consists essentially in treating *sodium chloride* with *ammonium hydrogen carbonate*, NH_4HCO_3.

$$NaCl + NH_4HCO_3 \longrightarrow NH_4Cl + NaHCO_3.$$

This reaction takes place because sodium hydrogen carbonate (*sodium bicarbonate*) is not very soluble in water and is, therefore, readily precipitated when *ammonium hydrogen carbonate* is added to concentrated salt solution. The solution of ammonium hydrogen carbonate is formed by passing carbon dioxide under pressure into a saturated solution of ammonia (NH_4OH).

$$NH_4OH + H_2CO_3 \longrightarrow NH_4HCO_3 + H_2O.$$

Gentle heating converts the bicarbonate into carbonate.

$$2\ NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The carbon dioxide thus set free is used again; and nearly all the ammonia is recovered by heating the brine, from which the bicarbonate has crystallized, with slaked lime (*cf.* § 142).

The **Le Blanc Process** consists of essentially *three* operations: —

(1) The conversion of common salt into *sodium sulphate* (*cf.* § 92):

$$2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HCl.$$

(2) The reduction of sodium *sulphate* to sodium *sulphide;*

$$Na_2SO_4 + 4\ C \longrightarrow Na_2S + 4\ CO.$$

(3) The conversion of sodium sulphide into the *carbonate;*

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS.$$

The *second* and *third* operations take place *together*, sodium sulphate being mixed with limestone and coal-dust and the mixture heated. The sodium carbonate cannot readily be separated from calcium sulphide because both are soluble. If limestone is present *in excess*, however, some of it is dissociated into quicklime (CaO) and carbon dioxide; the quicklime and the calcium sulphide form an insoluble compound.

Soda comes into the market as *calcined soda*, or *soda-ash*, containing no crystal-water, and as *crystallized soda*, or *sal sodae*, $Na_2CO_3 . 10\ H_2O$. Soda is used in great quantities in the manufacture of *glass* (*cf.* § 342) and of *sodium hydroxide* (§ 365).

368. Sodium Bicarbonate. — Sodium bicarbonate is prepared by treating the normal salt with carbonic acid (*cf.* § 210). The equation for its decomposition by heat is given in § 367. It is used in large amounts for baking powders, effervescing mixtures, "soda-water," and medicine.

369. Sodium Phosphate. — The common phosphate of sodium is *disodium hydrogen phosphate*, $Na_2HPO_4 . 12\ H_2O$; it is formed by adding sodium carbonate to phosphoric acid until the solution is slightly *alkaline*.

Phosphoric acid is *tribasic* (*cf.* § 304) and its *insoluble* salts are usually *normal*, e. g., Li_3PO_4, $Ca_3(PO_4)_2$, Ag_3PO_4; but its normal sodium salt (Na_3PO_4) is so readily *hydrolyzed* (*cf.* § 354) that it absorbs carbonic acid from the air.

$$2\ Na_3PO_4 + H_2CO_3 \longrightarrow 2\ Na_2HPO_4 + Na_2CO_3.$$

370. Sodium Chloride. — Sodium chloride, or *common salt*, occurs widely distributed. It makes up about 3% of sea-water, and is found in large deposits in Galicia (Austria), Germany, England, the United States, etc. In some places salt is mined as *rock-salt*, while in others the mixture of salt and earth is treated with water, the resulting brine being pumped to the surface and then evaporated. At Manistee, Mich., the brine is concentrated and the salt continuously separated in a "vacuum" boiler.

Sodium chloride crystallizes in colorless, transparent *cubes*, which *decrepitate* (*cf.* § 50) when heated. It is only a little more soluble in hot than in cold water (*cf.* § 59).

Salt is necessary to the life of man and other animals, the hydrochloric acid of the gastric juice being derived from it (*cf.* § 260). It is used in enormous quantities, not only as food, but as the *starting material* in the preparation of most compounds of *sodium* and of *chlorine*.

371. Sodium Nitrate. — Sodium nitrate, or *Chile saltpeter*, occurs in enormous quantities in the Atacama Desert, in Chile (*cf.* § 163). It is very deliquescent, and so cannot be used for gunpowder, etc. It is converted into *potassium* nitrate, which is *not* deliquescent (*cf.* § 164), and into nitric acid (*cf.* § 155). Sodium nitrate is also a constituent of artificial fertilizers. The crude salt is an important source of *iodine* (*cf.* § 273).

372. Other Sodium Salts. — *Sodium sulphate*, or "Glauber's Salt," $Na_2SO_4 \cdot 10\ H_2O$, is made from common salt and sulphuric acid (*cf.* § 92). It is made, also, from *magnesium sulphate* and salt.

$$MgSO_4 + 2\ NaCl \longrightarrow Na_2SO_4 + MgCl_2.$$

This salt is very *efflorescent* (*cf.* § 53): its principal use is as a substitute for soda in the manufacture of glass.

Sodium thiosulphate, $Na_2S_2O_3 \cdot 5\ H_2O$, has been described in § 194; and *sodium tetraborate* (borax) in § 347.

Sodium salts color the Bunsen flame bright yellow.

373. **Potassium.** — The element potassium is a constituent of many minerals; among these are *feldspar*, a double silicate of potassium and aluminum; *sylvite*, practically pure potassium chloride; *potash alum;* and *saltpeter.*

Potassium is present in all soils; it doubtless comes from the disintegration of feldspar and other rocks. Plants take up potassium compounds; hence the element is found (as the carbonate, *potash*) in plant ashes. When the ashes are extracted with water, potassium carbonate dissolves.

Potassium is made by the electrolysis of *potassium cyanide*, *hydroxide*, or *chloride.* It is a soft metal like sodium, but has a slightly bluish luster. It decomposes water, giving the *hydroxide* and *hydrogen.* The energy evolved in the reaction is so great that the escaping gas is set on fire.

The vapors of potassium and of all potassium salts color the flame violet. Potassium, like sodium, must be kept under *kerosene* or *ligroin* to protect it from moist air.

374. **Potassium Hydroxide.** — Potassium hydroxide, or *caustic potash*, is made by the action of the electric current upon a concentrated solution of *potassium chloride* (*cf.* § 365).

$$2\,KCl + 2\,H_2O \longrightarrow 2\,KOH + H_2 + Cl_2.$$

It may also be made from *potassium carbonate* and "milk of lime," i. e., *calcium hydroxide.*

$$K_2CO_3 + Ca(OH)_2 \longrightarrow 2\ KOH + CaCO_3.$$

Potassium hydroxide is a white, deliquescent solid. It is a powerful base. It absorbs carbon dioxide from the air, forming *potassium carbonate.*

375. Potassium Carbonate, or Potash. — Much potassium carbonate is prepared by the Le Blanc and Solvay processes from potassium chloride (*cf.* § 367). The crude substance is obtained from wood-ashes. *Anhydrous* potassium carbonate is a powerful *dehydrating agent* (*cf.* § 53).

Potash is used chiefly in making the *hydroxide* and *hard glass* (*cf.* § 342).

376. Potassium Nitrate. — Potassium nitrate (called, also, *saltpeter* and *nitre*) has already been described (*cf.* §§ 163 to 165). Most of that in use is made from *sodium nitrate* and *potassium chloride*, both of which are found in large deposits. The equation is given in § 164.

377. Potassium Chlorate. — Potassium chlorate results when chlorine is passed into a *hot*, concentrated solution of potassium hydroxide until the solution is saturated (*cf.* § 281).

$$6\ KOH + 3\ Cl_2 \longrightarrow 5\ KCl + KClO_3 + 3\ H_2O.$$

A *cheaper* way is to pass the chlorine into *hot* "milk of lime"; *calcium chlorate*, $Ca(ClO_3)_2$, is formed. This with *potassium chloride* gives *potassium chlorate* and *calcium chloride.*

$$Ca(ClO_3)_2 + 2\ KCl \longrightarrow 2\ KClO_3 + CaCl_2.$$

Potassium chlorate, being much less soluble in cold water than the other substances, *crystallizes out*, leaving the others in solution.

Like the nitrate, potassium chlorate is valuable chiefly as an oxidizing agent. It is used in preparing oxygen, explosive mixtures, e. g., *smokeless powder*, matches, and fireworks. It is sold by druggists as "potash" for sore throats.

378. Potassium Bromide (KBr) and Potassium Iodide (KI). — Potassium bromide and potassium iodide may be prepared by the action of *bromine* and *iodine*, respectively, upon potassium hydroxide. The equations are analogous to the one for the action of *chlorine* upon caustic potash.

$$6\ KOH + 6\ Br \longrightarrow 5\ KBr + KBrO_3 + 3\ H_2O.$$
$$6\ KOH + 6\ I \longrightarrow 5\ KI + KIO_3 + 3\ H_2O.$$

By evaporating the solution containing *bromide* and *bromate*, or *iodide* and *iodate*, to dryness, and then heating the residue sufficiently, we can decompose the bromate and the iodate just as we can the chlorate (*cf.* § 19).

$$2\ KBrO_3 = 2\ KBr + 3\ O_2.$$
$$2\ KIO_3 = 2\ KI + 3\ O_2.$$

Potassium bromide and iodide are made, also, by treating the bromide and the iodide of iron with potassium carbonate.

$$Fe_3Br_8 + 4\ K_2CO_3 \longrightarrow Fe_3O_4 + 8\ KBr + 4\ CO_2.$$
$$Fe_3I_8 + 4\ K_2CO_3 \longrightarrow Fe_3O_4 + 8\ KI + 4\ CO_2.$$

The iron compounds are formed by adding bromine and iodine, respectively, to moist iron turnings.

379. Ammonium. — The formation of ammonium salts by neutralizing acids with ammonium hydroxide has already been described (*cf.* § 148). The radical NH_4 has not been isolated because it decomposes into ammonia and hydrogen. One of the many arguments for its existence is the formation of *ammonium amalgam* by the action of a strong solution of ammonium chloride upon *sodium amalgam* (*cf.* § 364).

$$\underset{\text{sodium amalgam}}{\text{Na, Hg}} + \text{NH}_4\text{Cl} \longrightarrow \underset{\text{ammonium amalgam}}{\text{NH}_4\text{, Hg}} + \text{NaCl}.$$

Ammonium amalgam is a bulky, metallic mass resembling sodium amalgam. It decomposes readily into ammonia, hydrogen, and mercury.

380. Exercises.

1. Why does the electrolysis of an aqueous solution of sodium chloride give *sodium hydroxide* and *hydrogen* at the — electrode (*cf.* § 365)?
2. Write the equations showing how potassium carbonate is made by the Solvay process (*cf.* § 375).
3. All four substances given in the equation in § 372 are *soluble*. Explain under what conditions the reaction can take place.
4. Describe the preparation of ammonium chloride, nitrate, and sulphate, giving equations. How does ammonium nitrate behave when heated? Ammonium chloride?

5. What is the *source* of the ammonia of commerce?

6. How do you explain the fact that sodium bicarbonate solution reacts *alkaline?*

7. Which of the following gases would you dry with solid caustic potash: *ammonia*, *hydrogen sulphide*, *carbon monoxide*, *carbon dioxide*, *oxygen?*

CHAPTER XXV.

THE ALKALINE-EARTH METALS.

381. The Group. — The "alkaline-earth" metals are so called because they form the transition from the *alkalies* to the "earth" metals, such as *aluminum.* In this chapter we shall consider *glucinum* (or beryllium), *magnesium*, *calcium*, *strontium*, and *barium.* The most important is calcium.

382. Calcium (Atomic Mass, 40). — Calcium does not occur free; but its compounds are found in large quantities. The most abundant is the *carbonate*, $CaCO_3$; this occurs as *limestone*, *marble*, *chalk*, *calc-spar*, and *coral.* The *sulphate*, $CaSO_4$, the *phosphate*, $Ca_3(PO_4)_2$, and the fluoride, $CaFl_2$, are also important minerals.

The metal is obtained by heating *calcium oxide* with *carbon* in a stream of hydrogen in an electric furnace. It is a silvery solid. *It decomposes water* like sodium and potassium.

383. Calcium Oxide (CaO). — Calcium oxide is familiar to all as *lime*, or *quicklime.* It is made by heating calcium carbonate in large furnaces called *lime-kilns.*

$$CaCO_3 = CaO + CO_2.$$

Lime is a white, amorphous solid, fusible only at the temperature of the electric furnace. For its use in the Drummond, or lime, light see § 11. It absorbs water and carbon dioxide from the air, forming *air-slaked* lime, which consists of the carbonate and hydroxide. Lime is thus a good agent for removing water and carbon dioxide from gases (*cf.* § 223).

When lime is treated with a suitable quantity of water, the two unite to form a soft, dry powder. The operation is called "slaking"; and the product, *calcium hydroxide*, is called "slaked lime."

$$CaO + H_2O = Ca(OH)_2.$$

So much heat is evolved when water and lime unite, that lime improperly protected from water has been the cause of many fires.

384. Calcium Hydroxide $Ca(OH)_2$. — Calcium hydroxide is not very soluble, less than 1½ parts dissolving in 1,000 of water. The solution is *lime-water;* its uses have been considered in §§ 99 and 209. If more of the hydroxide is present then the water will dissolve, the liquid appears *milky* ("milk of lime"; *cf.* §§ 374 and 377).

Uses. — Calcium hydroxide is generally prepared from the oxide just before using. It is used to prepare *ammonia* (*cf.* § 142), the *hydroxides* of sodium and potassium (*cf.* §§ 365 and 374), *bleaching powder* (*cf.* §§ 88 and 279), *chlorates* (*cf.* § 377), *glass*, *mortar*, and *cements* (*cf.* § 389); to purify *sugar* and *illuminating gas* (*cf.* § 223); to remove hair from hides; to extract metals from their ores; as a *disinfectant* and *white-wash*, and in making *stearin candles*.

385. Calcium Chloride ($CaCl_2$). — Calcium chloride is usually made from *calcium carbonate* and *hydrochloric acid* (*cf.* § 203). The *anhydrous* substance (made by heating at 200° C.) is very *deliquescent*, and dissolves in water with evolution of heat. It is used as a *drying agent* (*cf.* § 53).

The *crystallized* chloride, $CaCl_2 . 6 H_2O$, *absorbs* heat when dissolving in water (*cf.* § 57), and when mixed with ice or snow may produce a temperature of — 40° C. A concentrated solution of calcium chloride freezes so much lower than one of sodium chloride that it is often used instead of brine as the cold bath in ice factories (*cf.* § 146).

386. Calcium Carbonate ($CaCO_3$). — As already stated (*cf.* § 211) calcium carbonate occurs in many forms and widely distributed. *Limestone*, *chalk*, *calcite*, and *marble* are found in large masses. *Aragonite* crystallizes in a form different from that of the other varieties, but has the same composition.

Limestone, the most abundant form of calcium carbonate, is *gray*, and often contains small crystals, but is always mixed with clay and other impurities. Limestone containing much clay is **marl**. Marl is used in making cement. Limestone is used as a *flux* (*cf.* § 266) in smelting iron, as a source of *lime*, and as building-stone. **Chalk** is used for making lime. Carpenters use it for *marking*. **Marble** is used for building purposes, as a source of lime, etc.

387. Calcium Sulphate ($CaSO_4$). — Calcium sulphate occurs principally as *gypsum*, $CaSO_4 . 2 H_2O$. *Alabaster* is a granular form of gypsum.

When gypsum is heated to 120° to 130° C. it loses about *three-fourths* of its crystal-water, and forms the white powder known as **Plaster of Paris.**

$$\underset{\text{gypsum}}{2\ CaSO_4(H_2O)_2} = \underset{\text{plaster of Paris}}{(CaSO_4)_2H_2O} + 3\ H_2O.$$

When this powder is mixed with enough water to form a paste it expands, and hardens to a mass with a smooth surface. Because of these properties plaster of Paris is used to make *casts*, as a wall finish, and as a cement. The union of the powder with water produces the crystalline compound.

$$(CaSO_4)_2H_2O + 3\ H_2O = 2\ CaSO_4(H_2O)_2.$$

Calcium sulphate is slightly soluble in water ; water containing it is *permanently* hard (*cf.* § 43). When a *soluble* carbonate is added to a solution of calcium sulphate, *calcium carbonate* is precipitated.

$$CaSO_4 + Na_2CO_3 \longrightarrow \mathit{CaCO_3} + Na_2SO_4.$$

Hence the "softening" of hard water by means of soda.

388. Calcium Phosphate, $Ca_3(PO_4)_2$. — Normal calcium phosphate occurs as *phosphorite;* combined with calcium chloride or fluoride it forms *apatite.* Important deposits of these minerals are found in Florida and South Carolina. Calcium phosphate is the chief inorganic constituent of bones (*cf.* § 292). Being *insoluble*, normal calcium phosphate is converted into the *primary* phosphate, $Ca(H_2PO_4)_2$, for use as a fertilizer (*cf.* § 307). The primary phosphate is commonly known as "soluble phosphate"; the mixture of the primary phosphate and calcium sulphate is called "superphosphate."

Phosphates Necessary for Plants. — To be fertile, soil must contain calcium phosphate, an essential plant food. When the crops are removed, part of the phosphate of that region goes with them; hence, phosphate must be returned to the soil if the land is to yield good harvests. If the crops are used as food for animals, part of the phosphate returns to the soil in manure; if not, other fertilizers must be used. Nature usually keeps a soil fertile by means of decaying vegetation, which forms with the soil "vegetable mould."

Fertilizers. — A *complete* fertilizer supplies *potassium*, *nitrogen*, and *phosphorus*. Most fertilizers, however, contain only one or two of these essentials.

Potassium is usually returned to the soil as the *sulphate* or *carbonate* (wood-ashes; *cf.* § 373); sometimes as *chloride.*

Nitrogen is frequently supplied as *ammonium salts*, or as *nitrates*, especially *sodium nitrate* (*cf.* § 371). Nitrogen is also contained in *guano.*

Phosphorus is contained in fertilizers chiefly as "soluble phosphate," which is obtained by treating phosphate rocks or bone-ash with sulphuric acid.

The dry residue left after the *waste products* of slaughter-houses, *e. g.*, tainted meat, bones, hoofs, etc., are deprived of fat, oil, and gelatine, makes a good fertilizer. The fat is used as soap-stock.

389. Mortar and Cement. — When a thick paste of slaked lime and water is exposed to the air it gradually "sets," *i. e.*, becomes ***dry*** and ***hard***. The chemical action that takes place consists in the escape of water and the absorption of carbon dioxide from the air.

$$Ca(OH)_2 + H_2CO_3 \ (i.\ e., H_2O + CO_2) \longrightarrow CaCO_3 + 2\ H_2O.$$

During the "setting" the mass contracts. In the making of mortar and cements this contraction is overcome by the use of ***sand***. Sand also makes the mortar more *porous*, so that carbon dioxide can penetrate farther and moisture escape more easily. Freshly plastered walls remain moist for some time because of the slow liberation of water by carbon dioxide. The complete change requires a long time.

When *limestone*, *magnesium carbonate*, and *clay* (aluminum silicate, *cf.* § 341) are heated together, there is formed a **cement** which slakes slowly and without much heat evolution; this cement has the valuable property of *hardening under water*. It is known as **hydraulic cement.**

Blast-furnace *slag* (*cf.* § 430) and some *anhydrous* silicates form with lime a similar cement.

Portland Cement is made by heating to a very high temperature an artificial mixture of calcium carbonate and clay.

390. Other Calcium Compounds. — Bleaching powder, $CaOCl_2$, has already been described in §§ 88 and 279. It was formerly supposed to be a mixture of *calcium hypochlorite*, $Ca(OCl)_2$, and *calcium chloride*, $CaCl_2$. Such a mixture would have the same quantitative composition as bleaching powder, and would give the same ***ions*** in solution.

Barium salts impart a *green* color to the Bunsen flame, and are poisonous. The *nitrate*, $Ba(NO_3)_2$, is used in making green lights, fireworks, etc. The *chloride*, $BaCl_2 . 2 H_2O$, is a white, crystalline solid. With a solution of a *sulphate* it forms the very insoluble *barium sulphate*, $BaSO_4$, and thus serves as a test for *SO_4 ions* (*cf.* § 189).

Strontium salts impart a *red* color to the flame. The *nitrate*, $Sr(NO_3)_2$, is used in pyrotechny for producing red lights. The hydroxide is used in refining beet-sugar.

392. Magnesium. — Magnesium occurs as the *chloride*, *carbonate*, and *silicate*. The metal is prepared by the *electrolysis* of the double chloride of magnesium and potassium. This occurs as the mineral *carnallite*, $MgCl_2 . KCl . 6 H_2O$.

Magnesium is a silvery, white metal with a high luster. It is light (S.G. 1.74), and oxidizes slowly in ordinary air. When heated in oxygen it burns with a bright flame, forming *magnesium oxide*, MgO (*cf.* § 23); in air it burns to the oxide and the *nitride*, Mg_3N_2 (*cf.* § 115). The metal does not decompose water at ordinary temperatures; it differs in this respect from *calcium*, *strontium*, and *barium*, and from the *alkali* metals.

Magnesium powder is used for *flash-lights* and in fireworks.

393. Magnesium Compounds. — *Magnesium oxide* (magnesia) is formed when magnesium burns and when the carbonate and hydroxide are heated. It is very *re-*

fractory, i. e., hard to melt, and is used for making *crucibles*, *cupels*, etc.

Magnesium chloride forms deliquescent crystals ($MgCl_2 . 6\ H_2O$). When its solution is evaporated to dryness, hydrochloric acid escapes. The residue consists chiefly of the *oxide*.

$$MgCl_2 + H_2O \longrightarrow MgO + 2\ HCl.$$

Magnesium sulphate, $MgSO_4$, is called "Epsom salts." It is found in many springs and in the mineral *kieserite*, $MgSO_4 . H_2O$. Kieserite changes in contact with water to the salt $MgSO_4 . 7\ H_2O$, which is the magnesium sulphate of commerce.

Magnesium carbonate, $MgCO_3$, occurs as the mineral *magnesite*, and, combined with calcium carbonate, in *dolomite*.

The *normal* carbonate is not precipitated by alkaline carbonates, owing to the ease with which it is *hydrolyzed* (*cf.* § 354); the precipitate consists of a *basic* carbonate. At the same time carbonic acid is set free.

$$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3 + 2\ NaCl.$$
$$MgCO_3 + 2\ H_2O \longrightarrow Mg(OH)_2 + H_2CO_3.$$

The basic carbonate is a mixture of the carbonate and the hydroxide.

Asbestos is a mixture of *calcium* and *magnesium silicates*.

394. Glucinum or Beryllium (Atomic Mass, 9.08.) — Glucinum (Gl) is a rare, white metal, resembling magnesium. Its compounds have a *sweetish* taste; hence the name *glucinum* (*cf.* glucose, glycerine, etc.).

395. The Group a "Natural Family." — The members of the *calcium* group, like the alkali metals, form a natural family of elements. This will be apparent from a comparison of some of the properties as given in the following table. Magnesium really forms with glucinum, zinc, cadmium, and mercury a separate division; but many of its properties ally it with the calcium group.

ELEMENT.	*Magnesium*	*Calcium.*	*Strontium.*	*Barium.*
ATOMIC MASS.	24	40	88	137
SPECIFIC GRAVITY.	1.7	1.6	2.5	3.6
CARBONATE DISSOCIATES; TEMPERATURE.	300° C.	600° C.	1100° C.	1400° C.
GRAMS OF HYDROXIDE SOLUBLE IN A LITER OF WATER AT 15° C.	0.009	1.32	18	50
HEAT OF FORMATION OF CHLORIDE; UNITS.	151	170	185	195

396. Exercises.

1. The temperature at which strontium and barium *carbonates* dissociate being very high (see table), suggest how to get the oxides of these metals more easily (*cf.* §§ 169 and 321). Write a *possible* equation.

2. Why do carpenters still use *chalk* instead of *crayon* for marking? Crayon consists of gypsum, etc.

3. *Magnesium* oxide unites with water much less readily than *calcium* oxide; how, probably, would *strontium* oxide compare with calcium oxide? With *barium* oxide?

4. Write and explain the ionic equation for the action of a solution of *ammonium carbonate*, $(NH_4)_2CO_3$, upon barium chloride solution.

5. How many grams of carbon dioxide can be obtained from 200 grams of pure Iceland spar (*cf.* § 211)? How many liters at 20° C. and 740 mm.?

CHAPTER XXVI.

ZINC, CADMIUM, AND MERCURY.

397. The Zinc Group. — The elements zinc, cadmium, and mercury are members of the *second group* of the periodic system. They are, however, much more closely related to magnesium than to the calcium group proper. Zinc and cadmium are very much alike, and are usually found together in nature; but mercury differs from them in some important respects. In the vapor state the molecules of all three contain one atom each (*cf.* § 255).

398. Zinc (Atomic Mass, 65.4). — Zinc generally occurs in combination as the *sulphide*, ZnS, the *carbonate*, $ZnCO_3$, and the *silicate*, Zn_2SiO_4. The metallurgy of zinc is simple. Its ores are generally *roasted* to convert them into *oxide*, ZnO, and the oxide is reduced by charcoal.

The reduction of zinc oxide takes place in retorts or furnaces; from these the metal distills over into condensers. At first the vapors condense as a powder (*zinc dust*); afterwards the metal condenses as a liquid, and is cast into plates and bars. The zinc thus obtained (called *spelter*) is not pure. Pure zinc is obtained by the electrolysis of zinc chloride.

399. Properties. — Zinc is a white, hard, and lustrous metal. In dry air it does not change; but ordinarily its luster is soon dulled by a covering of basic carbonate. At the ordinary temperature, zinc is *brittle;* but between 100° C. and 150° C. it can be rolled into sheets and drawn into wire. At higher temperatures it is so brittle that it can be powdered.

Zinc melts at 420° C., and boils at about 1000° C. When heated much above the melting-point, it burns to zinc oxide. Water does not affect the metal, even at 100° C. Hot solutions of alkaline hydroxides attack it, forming *zincates* and hydrogen (*cf.* §§ 48, 336, and 424).

$$Zn + 2\,KOH \longrightarrow K_2ZnO_2 + H_2.$$

Commercial zinc reacts readily with all the ordinary acids; but the purer the metal, the harder it is for acids to act upon it.

400. Uses. — Zinc is used for the positive plates of electric batteries and in **alloys,** e. g., *brass* (*cf.* § 409), *German silver*, etc.

Galvanized iron is iron coated with zinc by dipping it into a bath of molten zinc. Galvanized iron resists the action of air and moisture better than *tinned* iron. It is used for wire netting, corrugated roofing, gutters, water-tanks, etc.

401. Zinc Compounds. — Among the important zinc compounds are the *oxide*, *hydroxide*, *chloride*, *sulphate*, and *sulphide*.

Zinc oxide, ZnO, can be made by burning zinc, and by heating the carbonate or nitrate (*cf.* §§ 169 and 321). When hot it is *yellow;* when cold, *white.* It is sold as the pigment, **zinc white.**

Zinc chloride, $ZnCl_2$, may be formed by treating the metal with hydrochloric acid (*cf.* § 9). It is a white, deliquescent solid that fuses readily and distills without decomposing. It is usually cast in sticks.

Zinc sulphate, $ZnSO_4$, is formed from the metal and *dilute* sulphuric acid. Large quantities are made by roasting the natural *sulphide,* ZnS, and extracting with water.

$$ZnS + 2\ O_2 = ZnSO_4.$$

From water the sulphate separates as transparent crystals of "**white vitriol,**" $ZnSO_4 . 7\ H_2O$.

Zinc sulphide, ZnS, separates as a *white* precipitate when an alkaline sulphide is added to the solution of a zinc salt.

402. Cadmium. — The metal cadmium has the atomic mass 112.3. It is similar to zinc, melts at 320° C., and is used in making some *alloys* (*cf.* § 323). The *sulphide,* CdS, forms a beautiful, yellow pigment.

403. Mercury (Atomic Mass, 200). — Mercury, or *quicksilver,* occurs native in some of its ores; but the principal source of it is *cinnabar,* HgS. Cinnabar is mined chiefly in Spain and California; recently deposits have been found in Texas. Mercury is obtained from its ore by *roasting.* The sulphur passes off as sulphur dioxide; while the mercury vapors are condensed.

404. Properties and Uses. — Mercury is a white, lustrous liquid. It is 13.6 times as heavy as water; solidifies at — 39.5° C.; and boils at 357° C.

Mercury does not react with hydrochloric acid nor with *cold* sulphuric acid. Hot, concentrated sulphuric acid attacks it (*cf.* § 187); so does *nitric acid.* If the nitric acid is *dilute* and *cold*, and the mercury is *in excess*, the salt formed is *mercurous nitrate*, $HgNO_3$; if the *concentrated* acid is used, and the mercury is completely used up, *mercuric nitrate*, $Hg(NO_3)_2$, is formed. Both nitrates are white, crystalline solids.

Mercury vapor is very poisonous.

Mercury is used in extracting gold and silver from their ores, in amalgamating battery zincs, and in making thermometers, barometers, air-pumps, etc.

405. Mercury Compounds. — There are many interesting mercury compounds, but we shall consider only the *oxides*, mercuric and mercurous, the *chlorides*, and *mercuric sulphide.*

Mercuric oxide, HgO, also known as "red precipitate," may be made by long heating of the metal almost to its boiling temperature in contact with air. It is *usually* prepared by heating the *nitrate*, $Hg(NO_3)_2$ (*cf.* § 401; *zinc oxide*). An *isomeric* form (*cf.* § 262) is yellow in color; this is prepared by adding an alkaline hydroxide solution to the solution of a mercuric salt.

$$2\ NaOH + Hg(NO_3)_2 \longrightarrow 2\ NaNO_3 + HgO + H_2O.$$

The effect of heat upon the oxide is described in § 21.

Mercurous oxide, Hg_2O, is formed when an alkali is added to a *mercurous* salt.

Mercurous chloride, HgCl, is known as *calomel*, and is an important medicine. It is precipitated when a solution of a chloride is added to a solution of a mercurous salt.

It is commonly made by subliming a mixture of mercury and *mercuric* chloride,

$$Hg + HgCl_2 = 2\ HgCl.$$

Mercuric chloride, $HgCl_2$, is commonly called *corrosive sublimate.* It is made by subliming a mixture of *mercuric sulphate* and *sodium chloride.*

$$HgSO_4 + 2\ NaCl \longrightarrow HgCl_2 + Na_2SO_4.$$

Mercuric chloride is a white, crystalline solid; it is easily soluble in water, and very poisonous. It is used extensively in surgery (usually one part in 1,000 parts of water) because of its powerful antiseptic action.

Mercuric sulphide, HgS, occurs as *cinnabar* (§ 403), a red, crystalline substance. The sulphide may be made by rubbing together *mercury* and *sulphur*, and by passing *hydrogen sulphide* into the solution of a mercuric salt. In both cases the mercuric sulphide will be black; but when it is sublimed it yields *red* crystals. The red product is the pigment, "Chinese vermilion."

Sodium amalgam was mentioned in §§ 364 and 379. **Tin amalgam** was formerly used in making mirrors. **Zinc amalgam** is formed on the positive plate when battery zincs are "amalgamated." Several amalgams have been used for soft fillings by dentists.

CHAPTER XXVII.

COPPER, SILVER, AND GOLD.

406. Relation of Copper, etc., to the Alkali Metals — Copper, silver, and gold are in most respects different from the other members of the first periodic group, but are related to these elements — the alkali metals — much as zinc, cadmium, and mercury are related to the calcium group.

They are not changed by *water* or by *pure* air; hence they occur *native* as well as combined with other elements. Because they occur native all three have been known for thousands of years, while none of the alkali metals was known until 1807.

407. Copper (Atomic Mass, 63.6). — Copper is abundant and widely distributed. It occurs *native*, especially in the Lake Superior region, and in combination as *ruby copper*, Cu_2O; *malachite*, $CuCO_3 . Cu(OH)_2$; *chalcocite*, Cu_2S; and *copper pyrites*, $Cu_2S . Fe_2S_3$.

Of the world's supply of copper, the United States produces *more than half* (253,870 long tons in 1899). About 40% of this amount came from Montana, 26% from Lake Superior, and 23% from Arizona.

Native copper is obtained by crushing the ore, washing away lighter particles, and smelting and refining the concentrated "mineral." Lake Superior ore has from 0.75 of 1% to 5% of copper.

The **Arizona ore** consists of *hydroxide* and *carbonate*. It is smelted with coke in blast-furnaces, and often yields by one fusion a 96% copper.

Montana ores contain sulphur and iron. They are first *concentrated* by crushing and washing, and then *roasted* to remove most of the sulphur. Next they are *smelted* to form a "matte" containing 50% to 65% of copper, besides iron, sulphur, arsenic, etc.; then the molten matte is oxidized in a "converter" (*cf.* § 432, Fig. 63) by a blast of *hot air*, which removes sulphur and arsenic. Finally the product is cast into thick plates called "anodes," and refined by *electrolysis*.

408. Properties. — Copper has a red color, and is ductile and malleable. It melts at about 1080° C., while silver melts at 954° C. and gold at 1060° C. Copper is the best conductor of electricity known, except *silver; iron* is the only metal having greater tensile strength. The specific gravity of copper is 8.9.

In the atmosphere copper becomes coated with the basic carbonate (cf. *malachite*, § 407). The action of nitric acid and sulphuric acid upon copper has been discussed in §§ 159 and 187, respectively. Hydrochloric acid has practically no action upon it. Copper may be separated from solutions of its salts by *zinc*, *iron*, etc., and by *electrolysis*.

409. Uses. — Copper is used as an electric conductor, as ships' *sheathing* and *bolts*, and for electrical apparatus, utensils, coins, boilers, stills, etc. It is used, also, in *copper-plating* and *electrotyping*, and as a part of many *alloys.*

Brass usually contains 28% to 34% *zinc* and the remainder copper.

Bronze contains copper, zinc, and tin.

Gun-metal is about 90% copper and 10% tin.

Bell-metal consists of *copper*, about 75%, and *tin*, 25%.

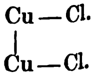
German silver is, *approximately*, 50% *copper*, 30% *zinc*, and 20% *nickel.*

Aluminum bronze is copper with 5% to 10% of aluminum. It has the color of gold, is hard and elastic, and does not tarnish easily. Aluminum containing 3% of copper is *whiter* than pure aluminum.

410. Copper Compounds. — Copper, like mercury, iron, etc., forms *two* series of compounds: *cuprous* and *cupric* compounds (*cf.* §§ 78 and 107). Examples are:

Cuprous chloride, $CuCl$ or Cu_2Cl_2.	*Cupric chloride*, $CuCl_2$.
Cuprous oxide, Cu_2O.	*Cupric oxide*, CuO.
Cuprous sulphide, Cu_2S.	*Cupric sulphide*, CuS.

In the *cupric* compounds copper is evidently *bivalent.* If copper is bivalent in the *cuprous* compounds of the halogens, *e. g.*, in *cuprous chloride*, the simpler formula must be doubled. The *graphic formula* for cuprous chloride will then be



$$\begin{array}{l} \mathrm{Cu - Cl.} \\ \;| \\ \mathrm{Cu - Cl.} \end{array}$$

Cuprous oxide occurs naturally as "ruby copper." It is formed as a black scale when the metal is heated in the air, and as a red precipitate when a solution of a cupric salt is heated with the solution of an alkali in the presence of a suitable reducing agent, e. g., *grape-sugar*, $C_6H_{12}O_6$.

Cupric oxide is formed by treating a boiling solution of a cupric salt with the solution of an alkali. The blue cupric *hydroxide*, $Cu(OH)_2$, which is formed if the solution is cold, cannot exist in the boiling solution.

$$CuSO_4 + 2\ KOH \longrightarrow K_2SO_4 + Cu(OH)_2.$$
$$Cu(OH)_2 \longrightarrow CuO + H_2O.$$

Cupric sulphate is known in crystalline form as *blue vitriol*, the formula of which is $CuSO_4 . 5\ H_2O$. When blue vitriol is heated, the water is expelled, and *anhydrous* cupric sulphate results. This is a white powder which becomes blue again in contact with water. Blue vitriol is used in making blue and green pigments, in copper-plating, in preserving wood, and for gravity batteries.

Cupric sulphide, CuS, is a heavy, black solid, precipitated when cupric salts in solution are treated with hydrogen sulphide or with alkaline sulphides.

411. Copper-plating. — An object that is to be plated with copper is put into a bath of some copper salt in solution, and connected with the *negative* electrode (kathode) of a battery or dynamo circuit. A bar of copper is used for the *positive* electrode (anode). The bar of copper is gradually used up, and copper is deposited upon the object to be plated. The bath does not deteriorate.

This process is used in making *electrotype plates*, either from type or from woodcuts. An impression of the type or woodcut is first made in plaster of Paris; this is covered with graphite powder and placed in the copper-plating bath as the *kathode.* The plate produced is an exact reproduction of the type or wood-cut from which the plaster impression was taken.

412. Silver (Atomic Mass, 107.94). — Silver is found native; also combined with sulphur and with the sulphides of other metals. The lead ore, *galena* (PbS), usually contains silver. The natural chloride, AgCl, is called "horn silver."

Most of the world's silver is found in the United States, Mexico, Bolivia, and Australia. The United States produced, in 1899, *54,764,500 ounces* — about one-third of the world's supply for that year.

413. Extraction of Silver from its Ores. — Silver is separated from its ores by various processes; we shall consider only *two*, viz., the *Amalgamation Process* and the *Smelting Process.*

The **Amalgamation Process** consists in extracting the metal with mercury, after a preparatory treatment. This treatment consists in *crushing* the ore, *roasting* it with salt to change the sulphide into the *chloride* of silver, and then reducing the chloride to silver by means of water and iron. The mass is then mixed with mercury, and the resulting *amalgam* is collected, dried, and heated in retorts. The mercury distills off, and is ready to be used again; the silver is then separated from whatever gold is present, as described at the end of this section.

Smelting Process. — Silver ores usually contain lead, and lead ores often have enough silver to pay for its removal; hence the reduction of the two metals is carried out in a single smelting operation.

The lead ore is *roasted* to remove sulphur, and then *reduced* with coke in a blast-furnace. The silver and the gold present remain alloyed with the lead. The resulting crude lead (known as **base bullion**) is then heated in a **reverberatory furnace** (Fig. 60), and stirred frequently. The small quantities of copper, arsenic, and antimony present are thus oxidized, and are skimmed from the surface as *dross*. What remains is a mixture of *lead*, *silver*, and *gold*. *Most* of the lead is now removed by the **Parkes Process**. This consists in melting the metal in large iron pots, adding 1% to 2% of **zinc**, and stirring. When the mixture is cooled slowly, an alloy of zinc, silver, and gold, with but little lead, comes to the surface, solidifies, and is skimmed off. If necessary, zinc is added a second or even a third time. The skimmings are then heated in **graphite** retorts (*cf.* § 198); and the zinc is distilled off, condensed, and cast into slabs to be used again. The residue in the retort consists of lead, silver, and gold. The lead is now completely removed from the precious metals by oxidizing it with hot air in a shallow furnace. The lead oxide (*litharge*, PbO) flows off from the top of the furnace.

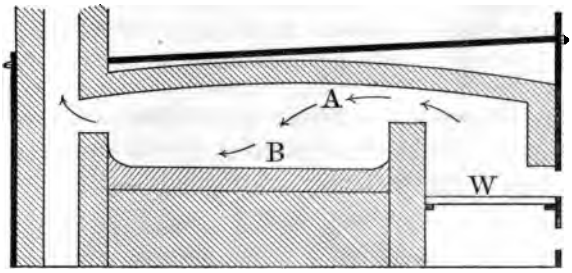


FIG. 60.

REVERBERATORY FURNACE.

(The fuel burns at *W*; the substance to be heated is placed on the hearth *B*. The curved roof *A* directs the hot gases of *W* down upon *B*.)

Gold is separated from silver by treating the mixture of these metals with nitric acid, or hot, concentrated sulphuric acid. The gold is not acted upon.

The sulphuric acid separation is carried out in iron kettles. The silver sulphate formed is treated, in solution, with copper, which precipitates *silver*. This is melted and cast into *ingots*.

414. Properties. — Silver is a white metal, capable of receiving a mirror-like polish. It conducts heat and electricity better than any other metal, and is malleable and ductile. It melts at 954° C., and boils in the oxy-hydrogen flame. Melted silver absorbs about twenty-two times its own volume of oxygen; when the silver solidifies, the gas is given off.

Silver does not tarnish in pure air, but is quickly blackened by sulphur compounds (*cf.* § 176). Hydrochloric acid does not attack it. Nitric acid and hot, concentrated sulphuric acid act upon it as upon copper (*cf.* §§ 159 and 187).

415. Uses. — Silver is used for *coinage*, tableware, jewelry, ornaments, and mirrors, and for *plating* other metals. Pure silver is very soft, and is therefore alloyed with copper. The silver coins of the United States and of France contain 90% silver ("coin silver"), and are said to be 900 *fine*. The grade 925 fine is called "sterling silver"; British silver coins are of this grade.

Silver-plating is usually done by electrolysis of the *double cyanide of silver and potassium*. A bar of silver forms the anode, and the object to be plated, the kathode (*cf.* § 411). The rough or "matt" surface is given the usual lustrous finish by polishing with chalk. The double cyanide solution is made by adding to a silver nitrate solution one of *potassium cyanide* (*cf.* § 215) until the silver cyanide first precipitated is redissolved.

Mirrors are made by precipitating silver upon glass. The silver is deposited from silver nitrate solution containing ammonia. This solution and a suitable reducing agent, *e. g.*, *ammonium tartrate*, or *acetaldehyde* (CH_3CHO), are put upon the glass, and the glass is gently heated. The bright deposit of silver is washed, dried, and covered with varnish to protect it from the hydrogen sulphide, etc., of the air.

416. Compounds of Silver. — *Silver nitrate*, $AgNO_3$, is the most important compound of silver. It is a white, crystalline solid, made by dissolving silver in dilute nitric acid. Silver nitrate is sometimes called *lunar caustic*.

Silver chloride, $AgCl$, *silver bromide*, $AgBr$, and *silver iodide*, AgI (*cf.* § 285), are made by adding solutions of chlorides, bromides, and iodides, respectively, to solutions of silver salts. They are affected by light, and are used in photography.

417. Photography. — Silver salts are used in photography because they change color and become insoluble in certain chemicals after being exposed to light. When a photographic plate is exposed in a camera, no change is visible until the plate has been **developed.** Developing consists in treating the plate with a *reducing* agent, such as *ferrous sulphate*, *pyrogallic acid*, *hydroquinone*, *eikonogen*, etc. When the plate is covered with the developing solution, an image appears; this is due to the precipitation of a film of ***silver***, which produces variations of light and shade. Where the light acted ***strongly*** upon the plate, the deposit of silver is relatively heavy; and where there was little action, there is little metal deposited.

Just what the action of light upon the silver bromide of a plate is, is not definitely known, but it certainly makes the reduction to silver take place more easily than is the case with *ordinary* silver bromide. The action of a developer may be illustrated by the following equation : —

$$2\ \text{AgBr} + \underset{\text{hydroquinone}}{C_6H_4(OH)_2} + 2\ \text{KOH} \longrightarrow$$

$$2\ \text{Ag} + 2\ \text{KBr} + 2\ H_2O + \underset{\text{quinone}}{C_6H_4O_2}.$$

In this case the *reduction* of the silver bromide is due to the **oxidation** of **hydroquinone** to **quinone.**

Fixing. — When the plate is sufficiently *developed*, it is rinsed and put into a bath of *sodium thiosulphate* ("hypo"; *cf.* § 194) to remove the silver salts not acted upon by light. This **fixes** the negative. The plate is called a "negative" because in it dark objects appear light, and light objects dark.

A "**print**" is made by placing the film of a sensitized paper next to the negative and exposing both so that the light passes through the negative. The image may appear on the paper *at once* ("printing-out" papers) or may have to be *developed* ("developing" papers). In either case the prints are "*fixed*" by removing the unchanged silver salt.

Toning. — Some papers are "**toned**" in a bath of *gold chloride*, $AuCl_3$, or *platinum chloride*, $PtCl_4$, before fixing. Toning replaces part of the silver by gold or platinum.

Blue prints are made on paper coated with a ***ferric salt*** (ferric ammonium citrate) and *potassium ferricyanide*, $K_3Fe(CN)_6$. After exposure, the picture is developed and fixed by washing it in water. The result is a blue print on a white ground. The process is used for copying *plans*, etc.

418. Gold (Atomic Mass, 197.2). — Gold is found both native and combined. Even *native* gold is not pure, however, but contains silver, and often iron, copper, etc. The metal is frequently found enclosed in *quartz* or *quartz-sand.*

Gold is obtained chiefly from Colorado and other western states, and from Australia, Siberia, and South Africa. The gold produced in the United States during 1899 was 3,437,210 fine ounces, worth $71,053,400. This was about *one-fourth* of the world's yield that year.

419. Metallurgy of Gold. — Gold-mining is of *two* general kinds: (1) *placer-mining*, and (2) *vein-mining.*

In **placer-mining** the clay and sand containing the gold are washed with water. The lighter particles are thus removed; while the gold and other heavy metals remain. Gold and silver are extracted from this mixture by mercury (*cf.* § 413; *amalgamation*).

Vein-mining consists in removing the gold-bearing rock from the earth and crushing it in stamp mills. The lighter materials are then washed away, and the gold is collected with mercury, as in placer-mining. **Hydraulic-mining** is a form of placer-mining done on a large scale with powerful streams of water.

Instead of mercury, **chlorine** and **bromine** are used to remove gold from the crushed ore. They form the soluble *gold chloride*, $AuCl_3$, or *bromide*, $AuBr_3$. This is extracted with water, and the gold is precipitated by means of *charcoal* or *ferrous sulphate* (*cf.* § 420).

The **Cyanide Process** depends upon the fact that gold is converted into the soluble double cyanide, KCN. AuCN, by a solution of the alkali cyanides. The gold is separated from the cyanide solution by electrolysis or by means of zinc.

420. Purification of Gold. — The gold obtained by the processes described above is not pure. It can be separated from silver by adding *aqua regia*, which reacts with the gold. The solution is evaporated to remove nitric acid, the residue is dissolved in water, and the gold is precipitated by *ferrous sulphate* or some other *reducing* agent.

$$3\ FeSO_4 + AuCl_3 \longrightarrow Fe_2(SO_4)_3 + FeCl_3 + Au.$$

In the treatment of silver and gold with sulphuric acid (*cf.* § 413, *end*) gold is left in the kettle as a brown, spongy mass. This is washed, dried, and melted in a crucible with charcoal and sodium carbonate. The resulting product, *chemically pure* gold, is poured into a mould, and leaves it as a *gold brick.*

421. Properties and Uses. — Gold is the only *common* metal that is yellow. It is a good conductor, and the most ductile and malleable substance known. Its specific gravity is 19.3, and its melting temperature 1060° C.

Gold unites directly with *chlorine* and *bromine*, but not with oxygen. *Aqua regia* reacts with gold, forming *auric chloride*, $AuCl_3$ (*cf.* § 417; "toning"); but the common acids do not affect it.

Gold is the *standard* of coinage of most nations. It is hardened by alloying it with copper (10% in the United States). For jewelry the proportion of gold aries from 40% to 75%; it is usually given as so many *carats fine.*" Pure gold is 24 carats fine; hence 18-arat gold is 75% gold and 25% alloy. Because of its *alleability* and weak chemical action, gold is much used y dentists for filling teeth. Gold-leaf is used in oramentation.

CHAPTER XXVIII.

ALUMINUM (Atomic Mass, 27).

422. Occurrence of Aluminum. — Although aluminum does not occur *free*, it is the most abundant and widely distributed metal. Only oxygen and silicon are more abundant. Some of the most important minerals containing aluminum are *feldspar* ($KAlSi_3O_8$), *mica* ($KAlSiO_4$), and *cryolite* (*cf.* § 266). *Granite* is a mixture of *quartz*, *feldspar*, and *mica*. *Clay* results when granite and similar minerals are decomposed.

All the other elements of the aluminum group are rare (*cf.* Periodic Table, § 332).

423. Preparation. — Aluminum was formerly produced from *anhydrous* aluminum chloride and sodium.

$$AlCl_3 + 3\,Na \longrightarrow Al + 3\,NaCl.$$

This method has been superseded by electrolytic processes, of which that of Hall (1887) is perhaps the most important.

Hall's Process. — The furnace used in the Hall process is a box of boiler iron (Fig. 61), the bottom and sides of which are lined with a mixture of coke and tar, rammed hard. The bottom forms the — electrode, while the + electrode consists of forty large carbons suspended by copper rods.

To begin the process, the carbons are lowered *almost* to the bottom of the furnace, *cryolite* is put in, and the current is turned on. The resistance to the passage of the current produces heat enough to melt the cryolite. Pure, dry *aluminum oxide*, Al_2O_3, is then mixed with the fused cryolite, and the electrolysis begins.

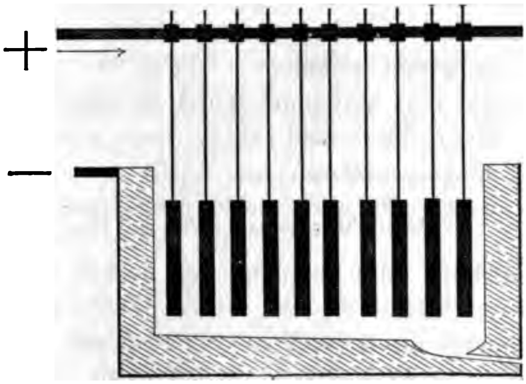


FIG. 61.

The process is **continuous,** for the cryolite bath remains unchanged. The aluminum collects at the bottom, and is drawn off ; the *oxygen* of the aluminum oxide unites with the carbons to form *carbon monoxide*, which escapes. One company getting its power from Niagara produced 3,190 tons of aluminum during 1900 ; this was about one-third of the world's output.

The aluminum oxide used is obtained from *beauxite* (or bauxite), $Al(OH)_3$. The natural mineral has impurities, *e. g.*, *iron*, *silicon*, etc. ; these are removed at present by fusing the beauxite with a little metallic aluminum.

424. Properties. — Aluminum is a white, lustrous metal. Its specific gravity (2.6) is very low compared with that of other common metals, zinc being 7.1 and [illegible] water. It melts at [illegible] the temperature [illegible] a good [illegible] and has the tensile strength [illegible] aluminum [illegible] aluminum [illegible] hydrochloric acid readily reacts with the metal, [illegible] aluminum chloride.

$$2\,Al + 6\,HCl \longrightarrow 2\,AlCl_3 + 3\,H_2.$$

Nitric acid and dilute sulphuric acid do not act upon it readily.

Aluminum reacts with solutions of salt and other chlorides if a little free acid is present. It reacts also with the hydroxides of sodium and potassium, forming *aluminates* and hydrogen.

$$6\,NaOH + 2\,Al \longrightarrow 2\,Na_3AlO_3 + 3\,H_2.$$

Aluminum unites directly with the *halogens*, and with *carbon*, *silicon*, *nitrogen*, etc.

425. Uses. — It is probable that more aluminum is used in the manufacture of iron and steel than for any other *one* purpose. The aluminum removes any oxygen the iron may have in combination, and thus increases the fluidity of cast-iron and steel.

The next important use is as a conductor of electricity. The Northwestern Elevated Railroad of Chicago is using twenty miles of 1½-inch aluminum cables, veighing 150,000 pounds, to transmit motive power to ts trolley cars.

Aluminum *powder* is used to reduce the oxides of many netals, e. g., *chromic oxide*, Cr_2O_3, and for flash-lights. A large art of the aluminum produced is used for kitchen utensils, cientific instruments, etc.; the aluminum **alloys** also require nuch of the metal.

The alloys with copper were described in § 409. A *new* lloy, called **magnalium**, contains 75% to 90% aluminum and the emainder *magnesium*.

426. Aluminum Oxide and Hydroxide. — Aluminum oxide, Al_2O_3, occurs in the form of *ruby*, *sapphire*, nd *corundum*. *Emery*, an impure form of corundum, s very hard, and is used for grinding and polishing. Aluminum oxide may be made by heating the *hydroxide*.

$$2\ Al(OH)_3 = Al_2O_3 + 3\ H_2O.$$

Aluminum hydroxide, $Al(OH)_3$, may be precipitated by adding *ammonium hydroxide* to the solution of an luminum salt, e. g., *aluminum chloride*. Aluminum hydroxide reacts with both acids and alkalies (except mmonium hydroxide); with acids it gives *aluminum alts*, and with alkalies, *aluminates* (*cf.* § 424). It is, herefore, a *base* toward strong acids and an *acid* toward trong bases (*cf.* §§ 312 and 317).

$$(1)\ Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O.$$
$$(2)\ H_3AlO_3 + 3\ NaOH \longrightarrow Na_3AlO_3 + 3\ H_2O.$$

Aluminum hydroxide unites either chemically or mechanially with many dye-stuffs, and also with certain fabrics. Advantage is taken of this fact to "**fix**" the dyes in fabrics that do not readily hold color. The hydroxide is therefore called a **mordant**, from Latin *to bite*, because it *bites into* the fabric.

427. Aluminum Salts. — *Aluminum chloride*, $AlCl_3$, is soluble in water, and crystallizes with crystal-water ($AlCl_3 . 6 H_2O$); but it is so much hydrolyzed that when the water is expelled hydrochloric acid escapes, and aluminum hydroxide remains.

$$AlCl_3 + 3 H_2O \rightleftarrows Al(OH)_3 + 3 HCl.$$

The *anhydrous* chloride is made by letting dry hydrochloric acid gas act upon *hot* aluminum filings. It is a hygroscopic, white powder.

Alums. — *Aluminum sulphate*, $Al_2(SO_4)_3$, forms double salts with the sulphates of *univalent* metals, *e. g.*, with *potassium sulphate*, K_2SO_4; these double sulphates are called *alums*. The alums crystallize with twenty-four molecules of crystal-water. *Potash-alum* is K_2SO_4, $Al_2(SO_4)_3$, 24 H_2O; *silver-alum* is Ag_2SO_4, $Al_2(SO_4)_3$, 24 H_2O. Other *trivalent* elements may replace aluminum. Thus Na_2SO_4, $Fe_2(SO_4)_3$, 24 H_2O would be *sodium iron-alum*. *Chrome-alum* is K_2SO_4, $Cr_2(SO_4)_3$, 24 H_2O.

Aluminum Carbonate and Sulphide. — The electro-positive properties of aluminum are so weak that even its salts with *strong* acids, *e. g.*, the *chloride* and *sulphate*, are readily hydrolyzed. Its salts with weak acids cannot exist in the presence of water, being completely decomposed into the *hydroxide* and the free acid.

When the acid is volatile, it of course escapes. This is the case with the *carbonate*. When aluminum salts are treated with the solution of a carbonate, the products are *aluminum hydroxide* and *carbonic acid*. Hence carbon dioxide escapes.

$$(1)\ 2\,AlCl_3 + 3\,Na_2CO_3 \longrightarrow Al_2(CO_3)_3 + 6\,NaCl.$$
$$(2)\ Al_2(CO_3)_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + 3\,H_2CO_3.$$

With the sulphide the result is similar.

$$(1)\ 2\,AlCl_3 + 3\,(NH_4)_2S \longrightarrow Al_2S_3 + 6\,NH_4Cl.$$
$$(2)\ Al_2S_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + 3\,H_2S.$$

428. Porcelain, Stoneware, Etc. — *Aluminum silicate*, $Al_2(SiO_3)_3$, is essentially the substance from which porcelain, etc., are made. In a pure form it is *kaolin;* in an impure form, *clay* (*cf.* § 341).

Porcelain is made by mixing white kaolin with more fusible substances, such as *feldspar*, shaping the plastic mixture into form, and heating it to a high temperature. The more fusible portion (the feldspar) melts, and cements the whole together. Porcelain is hard and translucent, and withstands the action of heat and chemicals better than glass, hence it is used for many purposes in chemical laboratories.

Stoneware is *opaque*, for it has not been heated enough to make the feldspar penetrate the kaolin as much as in porcelain.

Earthenware is made from common clay, hardened by heat, but not fused. It is glazed by putting common salt into the furnace at the time of heating. This forms a covering of sodium aluminum silicate over the porous surface. Bricks, tiling, jugs, terra-cotta, etc., are examples.

Ultramarine is a blue coloring substance, made by melting ogether *kaolin*, *sodium carbonate*, and *sulphur*. This substance was once very valuable, but thousands of tons of it are now made every year.

431. Commercial Iron. — The various grades of iron are *alloys* of the metal with more or less *carbon*, besides traces of silicon, sulphur, phosphorus, manganese, etc. The three chief subdivisions of the kinds of iron are *cast-iron*, *wrought-iron*, and *steel*.

Cast-iron contains from 1.5% to 7% of carbon. All the varieties of cast-iron melt comparatively low (1050° to 1250° C.), and are shaped by pouring them in the liquid state into sand moulds. Cast-iron is too *brittle* to be welded or forged.

Wrought-iron. — If the carbon of cast-iron is nearly all removed, the iron becomes tough and malleable, and requires a high temperature (1400° C. and above) to melt it. It can be *forged* and *welded*, but not *cast* or tempered. This form is *wrought-iron*. It usually contains 0.6%, or less, of carbon

Steel generally contains more carbon than wrought-iron, and less than cast-iron. It may be forged, welded, cast, and tempered. It melts higher than cast-iron and lower than wrought-iron.

Annealing and Tempering Steel. — If steel containing over 0.5% of carbon is heated to cherry redness and then quickly cooled in water or oil, it *hardens*, and is suitable for *cutting* tools, etc. If the hardened steel is slowly heated up again, and then slowly cooled, it becomes soft. This process is known as **annealing**. If, however, the hardened steel is heated up slowly until a film of a particular color appears, and is *then* plunged into water, it will retain a definite degree of hardness. This process is called **tempering**.

432. Manufacture of Steel. — Steel may be made (1) by removing part of the carbon from cast-iron, (2) by adding carbon to wrought-iron, and (3) by melting together cast- and wrought-iron. Method (1) is now rarely used; method (2) is applied in the *crucible* process of making steel; method (3) is the basis of the *Bessemer* and *Open Hearth* (Siemens-Martin) processes.

The **crucible** process consists essentially in heating a very pure wrought-iron with carbon for a long time. Some of the carbon is absorbed, producing a very fine quality of steel, suitable for tools. The process is, however, expensive.

The **Bessemer** process consists essentially in reducing pig iron in a "converter" to wrought-iron, and then adding enough cast-iron (called "spiegeleisen") to bring the proportion of carbon up to the desired point.

The **converter** (Fig. 63) is a large, pear-shaped furnace mounted upon supports (*S*) so that it can be inverted. A blast of air forced up through openings at the bottom (tuyères, *T*) oxidizes the silicon and carbon, the former to a slag, the latter to carbon dioxide. Manganese is put into the spiegeleisen to reduce any iron oxide formed, the resulting oxide of manganese separating in the slag. If the pig-iron contains much phosphorus and sulphur the converter is lined with quicklime and magnesia. The lining retains most of the phosphorus as phosphate.

Converters usually make ten to twenty tons of steel at a "blow." The time taken is about thirty minutes.

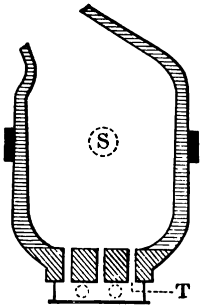


FIG. 63.

Bessemer steel contains about 0.35% carbon; it is used for rails, axles, cannon, wire, tin-plate, and structural purposes.

In the **Open Hearth** process, pig-iron is mixed with wrought-iron or steel scrap, and heated on a hearth with an *oxidizing* gas-flame. When the proportion of carbon has been lowered sufficiently, manganese is added in the form of "*spiegeleisen*" or "*ferro-manganese.*" The charge is usually about twenty tons; but the process takes from eight to eleven hours, and is consequently more expensive than the Bessemer process. Steel made in this way is, however, very tough and elastic, and is suitable for the finest structural work, e. g., *bridges*, and for machinery, boiler-plate, large guns, etc.

433. Properties of Iron. — Pure iron is rare; it melts at about 1800° C. The purest commercial form is wrought-iron; this is malleable, ductile, and a fairly good conductor. In the form of *steel*, iron may be made very hard.

Soft, i. e., *wrought*, iron may be magnetized *temporarily*, but soon loses the magnetism; steel is not so easily magnetized, but becomes a *permanent* magnet.

At a high temperature iron decomposes water vapor, yielding the oxide Fe_3O_4 and hydrogen.

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2.$$

When iron is burned in oxygen the same oxide results (*cf.* § 23). In dry air iron does not change, but in the presence of moisture and carbon dioxide it *rusts.* Iron rust is a mixture of *ferric oxide* (Fe_2O_3) and *ferric hydroxide*, $Fe(OH)_3$. Iron reacts easily with dilute acids. Two classes of iron compounds are known, viz., *ferrous* and *ferric* compounds (*cf.* §§ 78 and 107).

434. Oxides and Hydroxides of Iron. — *Ferrous oxide*, FeO, is not easily prepared or kept in pure condition.

It may be made by reducing ferric oxide with hydrogen at 300° C.; but on exposure to air it at once oxidizes.

Ferric oxide, Fe_2O_3, is found in enormous masses (hæmatite). It may be made by heating *ferric hydroxide* or *ferrous sulphate*.

$$2\ Fe(OH)_3 = Fe_2O_3 + 3\ H_2O.$$

Ferrous-ferric oxide, Fe_3O_4, is called the "magnetic oxide" of iron; it occurs as *magnetite*. It is sometimes found as *lodestone*, a natural magnet. Iron may be kept from rusting by exposing it while red hot to steam; the resulting layer of the black oxide, Fe_3O_4, protects the remainder of the metal.

Ferrous hydroxide, $Fe(OH)_2$, is formed when an alkali in solution is added to the solution of a *ferrous* salt. It is usually *green*, but soon becomes brown where air is in contact with it. In the absence of air it is white.

Ferric hydroxide, $Fe(OH)_3$, is made by adding an alkali or ammonia water to the solution of a *ferric* salt. It forms a flaky, red-brown precipitate.

435. Iron Sulphides. — *Ferrous sulphide*, FeS (*cf.* § 179), is a black solid made by heating a mixture of sulphur and iron, and by adding an alkali sulphide to a *ferrous* salt solution.

$$K_2S + FeCl_2 \longrightarrow FeS + 2\ KCl.$$

Iron pyrites (FeS_2) has the color of brass, and is called "fool's gold." For its behavior when heated, see § 178.

436. Iron Chlorides. — *Ferrous chloride*, $FeCl_2$, is made by passing hydrochloric acid gas over hot iron. A solution of it results when iron is treated with the acid. Like all *ferrous* compounds it oxidizes easily to the *ferric* condition.

In the presence of hydrochloric acid the oxidation produces *ferric chloride.*

$$4\ FeCl_2 + 4\ HCl + O_2 \longrightarrow 4\ FeCl_3 + 2\ H_2O.$$

If no acid is present, part of the iron is oxidized to ferric *salt*, and part to *ferric hydroxide* (rust).

$$12\ FeCl_2 + 3\ O_2 + 6\ H_2O \longrightarrow 8\ FeCl_3 + 4\ Fe(OH)_3.$$

Ferric chloride, $FeCl_3$, is formed in solution by passing *chlorine* into ferrous chloride solution, or by treating iron with *aqua regia*, and evaporating *repeatedly* with hydrochloric acid. The anhydrous salt is made by passing chlorine over red-hot iron. It looks like maple-sugar.

437. Iron Sulphates. — A solution of *ferrous sulphate*, $FeSO_4$, results when iron reacts with dilute sulphuric acid. The crystals known as *green vitriol* or "copperas" are $FeSO_4 . 7\ H_2O$. Green vitriol is used in making inks, in dyeing, and as a deodorizer. Ferrous sulphate is oxidized like the chloride. With ammonium sulphate it forms the *double salt*, *ferrous ammonium sulphate*, $(NH_4)_2SO_4 . FeSO_4 . 6\ H_2O$; this is much less easily oxidized than ferrous sulphate alone.

Ferric sulphate, $Fe_2(SO_4)_3$, is made, in solution, by oxidizing ferrous sulphate with nitric acid in the presence of sulphuric acid.

438. Potassium Ferro- and Ferri-cyanides. — *Potassium ferrocyanide*, $K_4Fe(CN)_6$, is called "yellow prussiate"

(i. e., *cyanide*, *cf.* § 216) "of potassium." It is a yellow, crystalline solid. With a ferric salt it produces *Prussian blue*. *Potassium ferricyanide*, $K_3Fe(CN)_6$, is obtained by oxidizing the ferrocyanide with chlorine. It is a *red*, crystalline solid.

Potassium *ferro*cyanide may be written $Fe(CN)_2 . 4\,KCN$; this formula shows that the iron is *ferrous*, i. e., bivalent. (Ferro- means *ferrous*.) In the *ferri*cyanide, $Fe(CN)_3 . 3\,KCN$, iron is in the *ferric* condition.

439. Nickel (Atomic Mass, 58.7). — Nickel occurs with iron in *meteorites*. Its ores (silicates of nickel) are found chiefly in Canada, Norway, and New Caledonia. Like iron, it forms *two* classes of compounds; these are *nickelous* and *nickelic* compounds. The common compounds are nickelous. Most of them are green. The formula of *nickel sulphate* is $NiSO_4$; that of the *nitrate*, $Ni(NO_3)_2$; that of the *sulphide*, NiS.

Nickel is used to plate other metals to protect them from the atmosphere. It is used, also, in making alloys, *e. g.*, German silver, nickel steel, and the United States five-cent piece. *Both nickel and cobalt are attracted by the magnet.*

440. Cobalt (Atomic Mass, 59). — Cobalt occurs combined with arsenic and sulphur, and often associated with nickel. Cobalt salts are *red* in solution or combined with much crystal-water, and *blue* when anhydrous or with little crystal-water. A solution of *cobaltous chloride*, $CoCl_2$, is used as a *sympathetic ink*.

CHAPTER XXX.

MANGANESE AND CHROMIUM.

441. Manganese (Atomic Mass, 55). — Manganese occurs chiefly as the *black oxide*, MnO_2, — the mineral *pyrolusite*. The pure metal is very hard, and fuses only at a high temperature. In some ways it resembles iron. Thus, it forms two series of salts, *manganous* and *manganic* salts, corresponding to *ferrous* and *ferric* salts. The manganous salts, however, are more stable than the ferrous salts, and are not readily oxidized. Manganic salts are much less stable than manganous salts. The latter are usually pink in color and crystalline. They are formed when the higher oxides of manganese are treated with acids, oxygen being either set free or else used in oxidizing the acid (*cf.* § 81).

442. Manganese Oxides. — Manganese forms the following oxides: —

Manganous oxide, MnO; *Manganese dioxide*, MnO_2;
Manganic oxide, Mn_2O_3; *Manganese heptoxide*, Mn_2O_7.
Manganous-manganic oxide, Mn_3O_4;

All of these are solids except the last, which is a dark liquid. The oxide Mn_2O_5, corresponding to the *manganates*, is not known.

The most important oxide of manganese is the *di-*

oxide. This is used in preparing chlorine and oxygen, and in decolorizing glass.

The manganese dioxide used in making chlorine is recovered by treating the manganous chloride produced (*cf.* § 81) with slaked lime. This forms *manganous hydroxide*, $Mn(OH)_2$. By means of steam, air, and more lime, this is converted into *manganites* having the formulas $CaMnO_3$ (*i. e.*, $CaO. MnO_2$) and $CaMn_2O_5$ (*i. e.*, $CaO. 2\ MnO_2$). Both of these give chlorine when treated with hydrochloric acid.

443. Potassium Permanganate. — Manganese forms not only *salts*, in which the manganese is the electropositive element, but also *manganates* and *permanganates*, in which the manganese has the same relation to the compound that *sulphur* has to the *sulphates.* The more highly oxidized the manganese is, the less basic does its oxide become. *Manganese heptoxide*, Mn_2O_7, is the anhydride of *permanganic acid*, $HMnO_4$; the most important salt of this acid is *potassium permanganate*, $KMnO_4$.

Potassium permanganate is formed by boiling the solution of the *manganate*, K_2MnO_4, and passing carbon dioxide or chlorine into it.

(1) $3\ K_2MnO_4 + 2\ CO_2 = 2\ K_2CO_3 + 2\ KMnO_4 + MnO_2$.
(2) $2\ K_2MnO_4 + Cl_2 = 2\ KCl + 2\ KMnO_4$.

The permanganate separates from solution in prisms. It colors water a deep purple. The manganate is obtained by fusing a mixture of manganese dioxide, potassium hydroxide, and an *oxidizing* agent, *e. g.*, potassium nitrate or chlorate.

A *crude* permanganate solution is used to oxidize sewage.

It is made by treating crude sodium manganate or potassium manganate with dilute sulphuric acid.

444. Oxidation by Permanganate. — Most of the uses of potassium permanganate are due to its easy liberation of oxygen. There is a difference depending upon whether it acts in *acid* or in *alkaline* solution.

We represent the oxidation of *oxalic acid* by potassium permanganate in the presence of sulphuric acid as follows: —

$$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 = 2\ MnSO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O.$$

Another process depends upon the oxidation of a *ferrous* to a *ferric* compound.

$$2\ KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 = 5\ Fe_2(SO_4)_3 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O.$$

Both of these reactions are sharp and complete, hence they have important uses in **volumetric analysis.**

To understand the oxidizing action of potassium permanganate in acid solution we must look upon this substance as made up of *potassium oxide* and *manganese heptoxide.*

$$2\ KMnO_4 = K_2O + Mn_2O_7.$$

The molecule of manganese heptoxide gives up *five* atoms of oxygen.

$$Mn_2O_7 = 2\ MnO + 5\ O.$$

The *manganous oxide* then reacts with the acid to form a manganous salt and water, and the *potassium oxide* to form a potassium salt and water.

$$MnO + H_2SO_4 = MnSO_4 + H_2O.$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O.$$

The *complete* equation is, therefore, —

$$2\ KMnO_4 + 3\ H_2SO_4 = 2\ MnSO_4 + K_2SO_4 + 3\ H_2O + 5\ O.$$

When the permanganate is used in *neutral* or *alkaline* solution, the available oxygen is less than in acid solution, *e. g.*, —

$$2\ KMnO_4 + H_2O = 3\ O + 2\ KOH + 2\ MnO_2.$$

If there is sufficient alkali, the manganese dioxide unites with it to form a *manganite*, e. g., K_2MnO_3, which remains in solution.

The action of potassium permanganate with *sulphurous acid* and with *hydrogen peroxide* is represented thus : —

$$2\ KMnO_4 + 5\ H_2SO_3 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 5\ H_2SO_4 + 3\ H_2O.$$
$$2\ KMnO_4 + 5\ H_2O_2 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ O_2.$$

445. Chromium (Atomic Mass, 52.1). — Chromium is a comparatively rare element. It occurs chiefly as *chromite*, $Fe(CrO_2)_2$ or $FeO.\ Cr_2O_3$. The name of the element is from the Greek *chroma*, meaning color. Chromium compounds have many decided colors.

The metal is prepared at a high temperature by reducing the oxide with carbon or the chloride with sodium. It is steel-gray, very hard, and very difficult to fuse. With iron it forms a hard alloy called "chrome-steel."

446. Oxides and Hydroxides. — The most important oxides of chromium are *chromic oxide* (Cr_2O_3) and *chromium trioxide* (CrO_3). *Chromous oxide*, CrO, is the one from which the *chromous* salts are derived.

Chromic oxide is a valuable pigment known as "chrome-green." It is made by driving off water from the hydroxide, $Cr(OH)_3$, or by heating a mixture of potassium dichromate, ammonium chloride, and sodium carbonate.

Chromium trioxide separates as bright red crystals when strong sulphuric acid is added to a saturated solution of potassium dichromate.

Although often called "chromic acid," it is really the *anhydride* of chromic acid, H_2CrO_4. It is a powerful oxidizing agent. Chromic acid is unknown.

Chromic hydroxide, $Cr(OH)_3$, is a green solid, formed when an alkaline hydroxide, carbonate, or sulphide is added to a chromic salt solution. It is soluble in an *excess* of the alkali, forming a *chromite* (*cf.* § 426). Chromites are derived from the substance having the formula $HCrO_2$; this is chromic hydroxide *minus* water. The carbonate and sulphide of chromium are decomposed by water, like the corresponding aluminum salts (*cf.* § 427).

447. Chromous and Chromic Salts. — Chromous salts are so readily oxidized that they are very hard to prepare. In this respect chromium differs decidedly from manganese, the corresponding salts of which, the *manganous* salts, are stable (*cf.* § 441). The chief chromic salts are *chromic chloride* ($CrCl_3$) and *chrome-alum*, $K_2Cr_2(SO_4)_4 \cdot 24\ H_2O$.

Chromic chloride is obtained as a beautiful, lavender-colored solid by passing chlorine over a mixture of chromic oxide and carbon. The carbon reduces the oxide, and, at the same time, chlorine unites with the chromium.

Chromic chloride is formed in solution by reducing a chromate or dichromate with alcohol, hydrogen sulphide, sulphurous acid, etc. The hydrated salt is green.

$$2\ K_2CrO_4 + 3\ H_2S + 10\ HCl = 4\ KCl + 2\ CrCl_3 + 8\ H_2O + 3\ S.$$

Chrome-alum is a violet-colored, crystalline substance, formed as a by-product in certain operations in which potassium dichromate is used as an oxidizing agent. It is analogous to ordinary alum, but contains chromium instead of aluminum (*cf.* § 427).

448. Double Nature of Chromium. — Chromium is not only a metal, but also an acid-forming element. Its *lower* oxides, like those of manganese, form salts with acids, and are, therefore, basic; but its higher oxides, especially the trioxide, CrO_3, are the anhydrides of acids.

The *chromites* formed by the reaction of chromic hydroxide with alkalies (*cf.* § 446) are not important; although *ferrous chromite*, $Fe(CrO_2)_2$, is the chief chromium ore. The *chromates* and the *dichromates*, however, are the most important chromium compounds. Chromium is in the same periodic group with sulphur; *chromic acid* (H_2CrO_4) corresponds with sulphuric acid and *dichromic acid*, $H_2Cr_2O_7$ or $H_2O.\ 2\ CrO_3$, with *fuming* or disulphuric acid, $H_2S_2O_7$.

449. Chromates and Dichromates.— *Potassium chromate*, K_2CrO_4, is made by roasting *chromite*, $Fe(CrO_2)_2$ or $FeO.\ Cr_2O_3$, with potassium carbonate and quicklime in the oxidizing flame of a reverberatory furnace (*cf.* Fig. 60). On a small scale the chromite is heated with a mixture of potassium nitrate and carbonate.

To understand the formation of the chromate we must think of it as made up as follows: —

$$2\ K_2O + Cr_2O_3 + 3\ O = 2\ K_2CrO_4.$$

The potassium *oxide* is present in the carbonate, the *chromic oxide* comes from the chromite, and the *oxygen* from the oxidizing agent or the air. In general, we change a chromic compound to a chromate by *oxidizing it in the presence of a base.*

Potassium chromate is yellow, like most chromates. Acids change it to *potassium dichromate*, $K_2Cr_2O_7$.

Potassium dichromate forms large, red crystals, which are soluble in about ten parts of water at the ordinary temperature. Alkalies change it to the chromate.

To understand the relation between the chromates and dichromates we must look upon their molecules as made up as follows : —

$$K_2Cr_2O_7 = K_2O.\ 2\ CrO_3.$$
$$K_2CrO_4 = K_2O.\ CrO_3.$$

Addition of alkalies, *e. g.*, potassium hydroxide, to the dichromate produces chromate.

$$K_2O.\ 2\ CrO_3 + 2\ KOH\ (i.\ e.,\ K_2O.\ H_2O) = H_2O + 2\ K_2CrO_4\ (i.\ e.,\ 2\ K_2O.\ CrO_3).$$

With acids, however, the reverse change takes place.

$$2\ K_2O.\ CrO_3 + H_2SO_4 = K_2O.\ 2\ CrO_3 + K_2SO_4 + H_2O.$$

Sodium dichromate, $Na_2Cr_2O_7$, is often employed in place of the potassium salt, owing to its greater solubility.

Both the chromates and the dichromates are used in dyeing, in calico-printing, and as oxidizing agents. Potassium dichromate is used in photography. Solutions of chromates and dichromates precipitate many metals, *e. g.*, lead, silver, and barium, as *chromates*.

450. Oxidation by Chromates and Dichromates. —

When a chromate or a dichromate is used as an oxidizing agent, the reactions are the reverse of those that take place when a chromate is synthesized: the chromate (or dichromate) is reduced in the presence of an acid to a chromic salt.

Thus we think of potassium chromate as breaking down into *potassium oxide*, *chromic oxide*, and *oxygen*.

$$2\ K_2CrO_4 = K_2O + Cr_2O_3 + 3\ O.$$

The oxygen is available for oxidation; while the oxides unite with the acids, giving salts.

If the acid present is sulphuric acid, potassium sulphate (K_2SO_4) and chromic sulphate, $Cr_2(SO_4)_3$, are formed. These unite to produce *chrome-alum*, $K_2Cr_2(SO_4)_4 \cdot 24\ H_2O$.

If, however, hydrochloric acid is present, we get a mixture of the chlorides of chromium and potassium. If there is no other reducing agent present, the nascent oxygen attacks the hydrochloric acid, giving chlorine and water.

$$K_2Cr_2O_7 + 14\ HCl = 2\ KCl + 2\ CrCl_3 + 7\ H_2O + 3\ Cl_2.$$

CHAPTER XXXI.

LEAD, TIN, AND PLATINUM.

A. Lead (Atomic Mass, 206.9.)

451. Occurrence and Preparation of Lead. — Lead occurs chiefly as *galena*, or *galenite*, PbS; and is obtained from it by the following process: —

The galena is first roasted in a reverberatory furnace (*cf.* Fig. 60). By this operation part of the ore is changed to the *oxide*, PbO, and part to the *sulphate*, $PbSO_4$, while some remains unchanged.

$$(1)\ 2\ PbS + 3\ O_2 \longrightarrow 2\ PbO + 2\ SO_2.$$
$$(2)\ PbS + 2\ O_2 \longrightarrow PbSO_4.$$

After the oxidation has gone far enough, the furnace doors are closed, and the mixture is heated without the admission of more air. The lead oxide and sulphate then react with the unchanged sulphide as follows: —

$$(1)\ PbS + 2\ PbO \longrightarrow 3\ Pb + SO_2.$$
$$(2)\ PbSO_4 + PbS \longrightarrow 2\ Pb + 2\ SO_2.$$

If the ores are poor, they are often heated with iron.

$$PbS + Fe = FeS + Pb.$$

If there is enough silver to pay for its extraction, the Parkes process is used (*cf.* § 413).

452. Properties and Uses. — Lead is soft, blue-gray metal having a high luster. It is malleable, but not very ductile. It melts at about 325° C.

Although lead is easily tarnished in the air, the corrosion does not penetrate, as with iron. Ordinary hard waters act but little upon lead; but soft waters containing *carbon dioxide*, *organic matter*, or much *chloride* or *nitrate*, attack it. Such waters should not be carried through lead pipes for household purposes.

All compounds of lead are poisonous.

Nitric acid acts readily upon lead, but hydrochloric and dilute sulphuric acids do not. Some metals, *e. g.*, zinc, separate lead from the solutions of its salts.

Lead pipes are used for conveying water and as sheaths for the cables of telephone wires. In sheet form the metal is used to line the "leaden chambers" (*cf.* § 184), and the sides and floors of vats and tanks where certain chemical processes are carried on. Large quantities of it are made into shot, bullets, type-metal, solder, pewter, and the plates of storage batteries.

453. Compounds of Lead. — Several *oxides* of lead are known. Among these are the *suboxide* (Pb_2O), the *monoxide* (PbO), the *dioxide* (PbO_2), and "*red lead*" or "minium," which is Pb_3O_4.

Lead monoxide, or "litharge," is formed by heating lead in a current of air. At 400° C. it takes up more oxygen, forming "**red lead,**" Pb_3O_4. When red lead is treated with dilute nitric acid, **lead dioxide** remains as a brown powder. Lead dioxide acts upon hydrochloric acid to give chlorine.

Lead nitrate, $Pb(NO_3)_2$, is made from litharge and nitric acid; *lead acetate*, $Pb(C_2H_3O_2)_2$, from litharge and acetic acid. Both are white, crystalline solids. Lead acetate is called "sugar of lead."

Lead sulphate ($PbSO_4$) and *lead chromate* ($PbCrO_4$) are insoluble in water. Lead chromate is called "chrome-yellow."

Lead chloride, $PbCl_2$, is difficultly soluble in cold water, but dissolves in hot water.

Lead carbonate, $PbCO_3$, is precipitated from solutions of lead salts by ammonium carbonate solution; the carbonates of sodium and potassium, however, give a *basic* carbonate instead.

Basic lead carbonate is made by various methods, and on a large scale; it is the pigment "white-lead." It forms a good paint, but turns brown or black in the presence of hydrogen sulphide.

Lead sulphide, PbS, is precipitated from the solution of a lead salt by soluble sulphides and by hydrogen sulphide.

Plumbites and Plumbates. — *Lead hydroxide*, $Pb(OH)_2$, reacts with alkalies, giving *plumbites*, e. g., K_2PbO_2; *lead dioxide* and alkalies give *plumbates*, e. g., K_2PbO_3. *Normal* plumbic acid would be H_4PbO_4 (*cf.* silicic acid, § 340). Its lead salt is Pb_2PbO_4, i. e., *red lead.*

B. Tin (Atomic Mass, 119.)

454. Occurrence and Preparation of Tin. — The only mineral abundant enough to serve as a source of tin is *cassiterite*, or tin-stone, SnO_2. This occurs in Cornwall (England), in Australia, in the island of Banca, and in the Black Hills.

Tin was known in very early times. Cassiterides was an ancient name for the Scilly Islands, owing to the fact that tinstone was found there. Although tin has been carried away from Cornwall since the times of the Phœnicians, the mines there are still producing it.

The metallurgy of tin consists, first, in *roasting* the ore, so as to oxidize and remove arsenic and sulphur. The tin oxide is then *reduced* with coal in a furnace, the metal being drawn off and cast into bars. These bars of impure tin are then slowly heated on a sloping hearth. The tin melts and runs down the hearth, leaving the unmelted impurities behind.

455. **Properties and Uses.** — Tin is a white metal having a brilliant luster. It does not lose its luster in the air. It is soft and malleable, and melts at about 227° C.

Tin reacts with hydrochloric acid, giving *stannous chloride*, $SnCl_2$. With concentrated sulphuric acid it gives *stannous sulphate*, $SnSO_4$, and sulphurous acid. Nitric acid oxidizes it to *metastannic acid* (H_2SnO_3).

The chief **use** of tin is to coat sheet-iron ; in this way the *tin-plate* of commerce is formed. It is also used to protect other metals, *e. g.*, copper and lead ; and in making *alloys*, *e. g.*, soft solder, pewter, bronze, bell-metal, etc.

456. **Compounds of Tin.** — Tin forms *stannous* and *stannic* compounds. Examples of the former are: *stan-*

nous chloride ($SnCl_2$), *stannous oxide* (SnO), and *stannous sulphide*, SnS. The corresponding *stannic* compounds have the formulas $SnCl_4$, SnO_2, and SnS_2. *Stannic acid*, like metastannic acid, is H_2SnO_3.

Stannous chloride is easily oxidized to stannic chloride, and is, therefore, a good *reducing agent*. Thus, it reduces *mercuric* chloride to *mercurous* chloride, and even to mercury.

$$(1)\ 2\,HgCl_2 + SnCl_2 = SnCl_4 + 2\,HgCl.$$
$$(2)\ 2\,HgCl + SnCl_2 = SnCl_4 + 2\,Hg.$$

Stannic chloride is a liquid. It is made by heating tin in chlorine. A solution of it is obtained by treating tin with aqua regia.

Stannic oxide is made when stannic acid is heated, and when tin is burned in the air. This oxide shows its acid character, and its analogy to carbon dioxide, silicon dioxide, and lead dioxide, by reacting with molten alkalies to form *stannates*, e. g., sodium stannate, Na_2SnO_3.

Stannous sulphide is a brown powder, formed when tin-foil is heated with sulphur, and when hydrogen sulphide is passed into the solution of a stannous salt.

Stannic sulphide separates as a yellow precipitate when hydrogen sulphide is passed into a stannic salt solution.

Both sulphides react with alkaline sulphides, forming *sulphostannates*, which are soluble in water (*cf* §§ 314 and 318).

C. Platinum (Atomic Mass, 195).

457. Occurrence and Preparation. — Platinum is found *native* in a few places, chiefly in western Siberia.

Native platinum is usually mixed with five other rare metals, all belonging to the **eighth** periodic group. These are:

palladium, ruthenium, rhodium, osmium, and iridium. About 75% of the ore is platinum.

The ore is treated with aqua regia, which reacts with the platinum and some iridium. The resulting *chlorplatinic acid*, H_2PtCl_6 (*cf.* bottom of page), is treated with ammonium chloride, producing a precipitate of *ammonium chlorplatinate*, $(NH_4)_2PtCl_6$. When this is heated strongly, metallic platinum results. The small quantity of iridium is not removed.

458. Properties and Uses. — Platinum is a grayish-white metal, over *21* times as heavy as water. Air has no action upon it; and the temperature of the oxy-hydrogen flame is needed to melt it.

Platinum is not attacked by the common acids; but it reacts with aqua regia and with chlorine- and bromine-water. Fused alkalies also act upon it.

The resistance of platinum to most chemicals and the high temperature at which it fuses make it very useful in the laboratory. It is used in the form of foil, crucibles, wire, and other utensils. Large retorts of platinum are used in concentrating and distilling sulphuric acid (cf. § 185).

459. Chlorplatinic Acid. — When platinum is treated with aqua regia, the platinum chloride ($PtCl_4$) formed unites with hydrochloric acid, giving chlorplatinic acid, H_2PtCl_6. The solution of this substance gives with potassium salts and with ammonium salts precipitates of *potassium chlorplatinate*, K_2PtCl_6, and of *ammonium chlorplatinate*, $(NH_4)_2PtCl_6$, respectively. The corresponding sodium salt is soluble.

CHAPTER XXXII.

SOME CARBON COMPOUNDS.

460. Organic Chemistry. — It was formerly believed that the complex substances produced by animals and plants, such as sugar, starch, uric acid, etc., could not be made in the chemical laboratory; hence there arose a distinction between "*organic*" and "*inorganic*" compounds. Organic compounds, it was thought, needed "vital energy" for their formation, while inorganic substances could be made without the intervention of living things. However, the synthesizing of *urea*, $CO(NH_2)_2$, an animal product, by Wöhler in 1828 and the many organic syntheses made since that time have destroyed the force of this distinction. At the present time the term "Organic Chemistry" is practically equivalent to "Chemistry of the Carbon Compounds."

The carbon compounds exceed in number those of all the other elements together, yet each substance is composed of relatively few elements. Many compounds contain only carbon and hydrogen; a much larger number, carbon, hydrogen, and oxygen. Many important organic substances contain carbon, hydrogen, and nitrogen, while others have oxygen in addition. Phosphorus, sulphur, and the halogens are also present in many organic compounds.

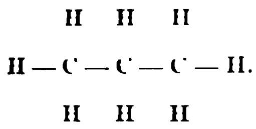
The compounds described in this chapter are classified as (1) hydrocarbons, (2) alcohols, (3) ethers, (4) aldehydes, (5) acids, (6) organic salts, or esters, (7) amines and alkaloids, (8) carbohydrates, and (9) phenol derivatives.

461. Hydrocarbons of Marsh Gas Series. — Substances composed of only hydrogen and carbon are called *hydrocarbons*. Several have already been mentioned in §§ 217 to 223. *Methane* (§ 217) is the first member of a large series — the **marsh gas**, or **paraffin series** — in which the formula of each member differs from that of the next member by CH_2. Such a series is said to be *homologous*.

The names and formulas of some members of the paraffin series are given in the first column of the table on page 408. The formulas show that the number of hydrogen atoms in the molecule of each of these hydrocarbons is two more than twice the number of carbon atoms; hence the series may be represented by the *general formula* C_nH_{2n+2}.

To explain the fact that so large a number of marsh gas hydrocarbons exists, chemists have assumed that carbon is *tetravalent* in these compounds (*cf.* §§ 259 and 260), and that the carbon atoms are *united in chains*.

The graphic formula for marsh gas has been given (*cf.* § 261). That of *ethane* is —



$$\begin{array}{ccccccc} & & H & & H & & H \\ H & — & C & — & C & — & C & — H. \\ & & H & & H & & H \end{array}$$

[illegible]	[illegible]	ACETYLENE SERIES.	POLYMETHYLENE SERIES.	BENZENE SERIES.
[illegible]				Benzene, C_6H_6.
[illegible]	[illegible]	Acetylene, C_2H_2.		Toluene, C_7H_8.
[illegible]	[illegible]	Allylene, C_3H_4.	Trimethylene, C_3H_6.	Xylene, C_8H_{10}.
[illegible]	Butylene, C_4H_8.	Crotonylene, C_4H_6.	Tetramethylene, C_4H_8.	Mesitylene, C_9H_{12}.
[illegible]	Amylene, C_5H_{10}.		Pentamethylene, C_5H_{10}.	
[illegible]	Hexylene, C_6H_{12}.		Hexamethylene, C_6H_{12}.	

The highest known member of the marsh gas series has the formula $C_{60}H_{122}$. The members from pentane to [illegible], $C_{15}H_{32}$, are liquids at ordinary temperatures: those of greater molecular mass, solids.

462. Ethylene and Acetylene Series. — As we learned in § 220, ethylene can unite with chlorine and bromine directly; it can also take up hydrogen, producing *ethane*.

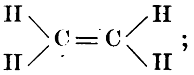
$$C_2H_4 + H_2 \longrightarrow C_2H_6.$$

The molecule of acetylene can take up **twice** as much of these substances as the molecule of ethylene.

$$C_2H_2 + 2H_2 \longrightarrow C_2H_6.$$
$$C_2H_2 + 2Br_2 \longrightarrow C_2H_2Br_4.$$

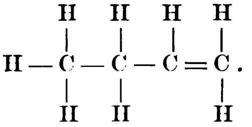
Because of their ability to unite with hydrogen, etc., to form marsh gas derivatives, both ethylene and acetylene are said to be *unsaturated,* to distinguish them from methane and its homologues, which are *saturated.* We explain the unsaturation existing in these compounds by assuming that all the valences of the carbon atoms are not used.

Ethylene is represented by the graphic formula



acetylene by $H - C \equiv C - H$.

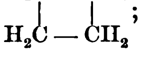
The homologues of ethylene and acetylene contain chains of carbon atoms with both saturated and unsaturated groups. Thus, the graphic formula of *butylene* (see table) is



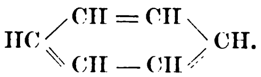
$$\begin{array}{ccccccccc} & & H & & H & & H & & H \\ & & | & & | & & | & & | \\ H & - & C & - & C & - & C & = & C . \\ & & | & & | & & & & | \\ & & H & & H & & & & H \end{array}$$

463. Closed and Open Chains. — The chains of carbon atoms in substances already described are called "open" chains to distinguish them from groups of atoms in *rings,* which are called "closed" chains. The *polymethylene* and *benzene* derivatives named in the table contain closed chains.

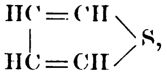
Thus, the graphic formula of *tetramethylene* is



that of *benzene*,



In *thiophene*,



a sulphur atom forms part of the ring.

464. Benzene Hydrocarbons. — In § 223 it was stated that benzene is obtained from coal tar. When the coal tar is distilled it yields several *fractions* the lower of which contain benzene and toluene, while higher-boiling portions consist of *xylene*, *naphthalene*, *anthracene*, etc.

Benzene is a colorless, aromatic liquid which boils at 80° C. and does not mix with water. It burns with a smoky flame. Solid benzene melts at 6° C. Benzene is used as a solvent and as a source of benzene derivatives, chiefly *nitrobenzene*, $C_6H_5NO_2$ (*cf.* § 165).

Nitrobenzene is a yellow liquid boiling at 205° C. It has the odor and taste of bitter almonds.

Toluene is *methylbenzene*, $C_6H_5CH_3$. It boils at 110°.

Naphthalene, $C_{10}H_8$, is a white solid melting at 79° and boiling at 218°. It is used for "moth balls" and in the preparation of dyes. It reacts with bromine according to the equation,

$$C_{10}H_8 + Br_2 \longrightarrow C_{10}H_7Br + HBr.$$

This is a good laboratory method for generating hydrobromic acid (*cf.* § 271).

Anthracene, $C_{10}H_{14}$, is a white solid melting at 213° and boiling about 350°. It is used as a source of the valuable red dye *alizarin*, which occurs naturally in madder root.

Turpentine is a resinous substance obtained from incisions in the bark of pines. By distillation it yields *oil of turpentine*, which consists largely of a hydrocarbon, $C_{10}H_{16}$ (*cf.* § 87). The residue is *rosin*.

465. Petroleum. — Petroleum is a thick, oily liquid obtained from the earth in many places. It consists essentially of a mixture of hydrocarbons, with larger or smaller amounts of nitrogen and sulphur compounds. The largest deposits are in the United States and Russia, but it occurs also in Japan, India, and Austria. In 1904 the United States produced about 110,000,000 barrels of the crude oil, valued at about $100,000,000.

It is uncertain how petroleum was produced, whether by the decomposition of animal or plant remains or by the action of water, under great pressure, upon *carbides*, particularly the carbide of iron.

Aluminum carbide and water react according to the equation,

$$Al_4C_3 + 12\ H_2O \longrightarrow 4\ Al(OH)_3 + 3\ CH_4.$$

Refining. — Some crude petroleum is used as a fuel and to enrich water-gas (*cf.* § 224), but most of it is *refined*. The petroleum is carried from the wells to the refineries through long systems of pipes. In the refining process it is shaken successively with sulphuric acid, caustic soda or potash solution, and water. It is then distilled, and the distillates which pass over between certain degrees of temperature are collected by themselves. Thus many *fractions* are obtained. The lowest fraction boils about 18° C., and is called *rhigolene*. This is used as a refrigerating agent. Between 18° and 250° *gasoline*, *benzine* (**not** benzene), *petroleum ether*, *kerosene*, etc., are collected. They are used as fuels and solvents. The higher-boiling products are converted into mineral lubricating oils, *vaseline*, and *paraffin* (white wax). Coke remains in the retort. Over two hundred commercial products are now made from petroleum.

466. Natural Gas. — In many places a combustible gas has collected in large, underground "pockets," and is released by drilling wells. The gas consists largely of *methane* (*cf.* § 218), and is carried to consumers in pipes, as in the case of illuminating gas. The value of the natural gas produced in the United States in 1903 was nearly $36,000,000.

467. Alcohols. — The alcohols form a large and important class of organic substances, and include several homologous series. The first member of one of these series is *methyl alcohol*, CH_4O, and its second member is *ethyl alcohol*, C_2H_6O. Methyl alcohol is called "wood spirit," because it is obtained in the dry distillation of wood (*cf.* § 201). It boils at 66° C. Ethyl alcohol boils at 78° C. Both are colorless liquids.

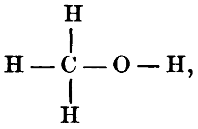
The alcohols react with metals much as water does (*cf.* § 46). Thus, ethyl alcohol and sodium produce *sodium ethylate* and hydrogen.

$$2\ C_2H_6O + 2\ Na \longrightarrow 2\ C_2H_5ONa + H_2.$$

With acids the alcohols react like hydroxides of the metals, giving *salts* and water.

$$CH_4O + HNO_3 \longrightarrow CH_3NO_3 \text{ (methyl nitrate)} + H_2O.$$
$$2\ C_2H_6O + H_2SO_4 \longrightarrow (C_2H_5)_2SO_4 \text{ (ethyl sulphate)} + 2H_2O.$$

These equations are like those for the reactions of potassium and sodium hydroxides with the acids (*cf.* §§ 100 and 158), consequently the alcohols are looked upon as *hydroxides.* The formula of methyl alcohol is, therefore, written CH_3OH, or



$$\begin{array}{c} H \\ | \\ H - C - O - H, \\ | \\ H \end{array}$$

and that of ethyl alcohol, C_2H_5OH (*cf.* § 262). The group CH_3 is the **radical** "methyl" (*cf.* § 148), and methyl alcohol is *methyl hydroxide.* The radical C_2H_5 is called "ethyl."

Some properties of the first five alcohols of the series are given in the table.

ALCOHOL.	FORMULA.	BOILING POINT.	SPECIFIC GRAVITY AT 20° C.
Methyl	CH_3OH	66°	0.796
Ethyl	C_2H_5OH	78°	0.789
Propyl	C_3H_7OH	97°	0.804
Butyl	C_4H_9OH	117°	0.810
Amyl	$C_5H_{11}OH$	138°	0.817

Both ethyl and methyl alcohols burn with colorless, hot flames. They mix with water, dissolve fats, oils, and gums, and are used in the manufacture of dyestuffs and varnishes. Ethyl alcohol is used as a solvent in the preparation of essences, extracts, perfumes, and medicines. It is also used to preserve anatomical specimens.

Ethyl alcohol solidifies at —112.3° C. and is used for thermometers reading below the freezing point of mercury (—40°).

468. Preparation of Ethyl Alcohol. — As already stated in § 206, *a*, alcohol is formed by the fermentation of sugar. Before cane sugar can be fermented it must be changed to grape sugar (*cf.* § 483). The agent of alcoholic fermentation is ***zymase***, a ferment present in yeast.

To prepare alcohol on a large scale starchy substances, such as potatoes, grains, rice, etc., are allowed to sprout and develop far enough to change much of their starch into sugar. This is then fermented by adding yeast. Besides alcohol and carbon dioxide, small amounts of *glycerine* and of *propyl*, *butyl*, and *amyl* alcohols are formed. The mixture of these alcohols is called **"fusel oil."**

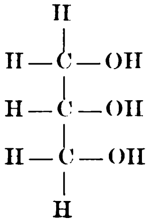
The ethyl alcohol is separated from most of the water and fusel oil by distillation, but the product ("95 per cent" alcohol) still contains from *four* to *ten* per cent of water. This may be almost entirely removed by distilling the commercial alcohol with lime. The distillate is called *absolute* alcohol.

469. **Liquors.** — Wines are prepared by allowing the ferments present in the air (*cf.* § 114) to act upon the juice of grapes. Beers are produced in a similar way from hops and malt (sprouted barley). When the fermented solution contains from 10 to 14% alcohol, action of the yeast ferment stops entirely. Liquors containing a larger proportion of alcohol have been distilled, or the alcohol has been added directly. The colors and flavors of liquors are due to substances present before fermentation or produced while the liquor stands in casks, or to foreign substances added.

Beer has ordinarily from 3 to 7% of alcohol; wine, 5 to 20%; and whiskey, gin, and rum, above 40%. In dilute form, alcohol acts as an intoxicant; undiluted, it is a poison.

470. **Glycerine.** — $C_3H_8O_3$. — Glycerine is a sweet, colorless, viscous liquid produced by the hydrolysis of fats (*cf.* §§ 366 and 480). It is soluble in alcohol and in water and absorbs moisture from the air. It is used in making nitroglycerine (*cf.* § 165), soaps, cosmetics, and inks; also as a food preservative and a lubricator. It boils at 290° C.

Glycerine is a complex alcohol. Its graphic formula is



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{H} \end{array}$$

471. Ethers. — If R represents an organic *radical*, ROH is the *general formula* of an alcohol (*cf.* table, § 467). We represent an *ether* by R—O—R, or R_2O. If the R of R_2O is CH_3, we have the formula of *methyl ether;* if C_2H_5, that of *ethyl ether.* For methyl ether see § 262.

Ethyl ether, $(C_2H_5)_2O$, is also called "sulphuric ether." It is a colorless, volatile liquid having a sweet odor. It boils at 35° C., is *very inflammable,* and is an excellent solvent for organic compounds. Ether is used in surgery as an anæsthetic. For its solubility in water see § 134.

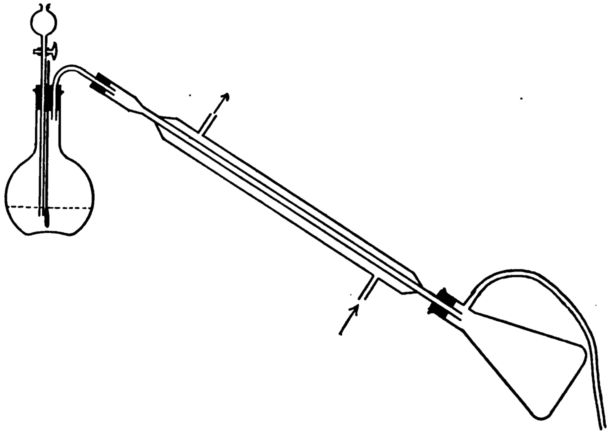


FIG. 64.

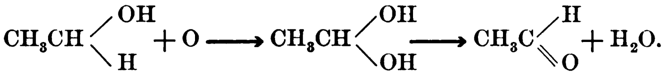
Preparation. — Ether is made in the laboratory (Fig. 64) by heating a mixture of ethyl alcohol and sulphuric acid to 140° (*not higher*) and keeping it at this temperature while adding alcohol in a slow stream through a separatory funnel.

The mixture of alcohol and ether which distills off is redistilled carefully. The rubber tube attached to the receiver (see Fig. 64) carries any uncondensed vapor of ether away from flames. The equations are:

1. $C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5HSO_4 + H_2O.$
2. $C_2H_5OH + C_2H_5HSO_4 \longrightarrow (C_2H_5)_2O + H_2SO_4.$

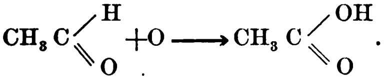
$C_2H_5HSO_4$ is *ethyl hydrogen sulphate* (*cf.* § 103).

472. Aldehydes. — The oxidation of ethyl alcohol by a mixture of potassium dichromate and dilute sulphuric acid produces acetaldehyde, CH_3CHO; called, also, simply *aldehyde.*



$$CH_3CH\begin{matrix}\diagup OH\\ \diagdown H\end{matrix} + O \longrightarrow CH_3CH\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} \longrightarrow CH_3C\begin{matrix}\diagup H\\ \diagdown\!\!\diagdown O\end{matrix} + H_2O.$$

Aldehyde is a colorless liquid boiling at 21° C. and very soluble in water. It is reduced by atomic hydrogen (*cf.* § 254), giving *ethyl alcohol.* With oxidizing agents it gives *acetic acid.*



$$CH_3\,C\begin{matrix}\diagup H\\ \diagdown\!\!\diagdown O\end{matrix} + O \longrightarrow CH_3\,C\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown O\end{matrix}.$$

Aldehyde is used to reduce silver solutions containing ammonia, as in the "silvering" of mirrors (*cf.* § 415). The name "aldehyde" is derived from *al(cohol) de hyd(rogenatus)*, i. e., "alcohol deprived of hydrogen."

Formaldehyde, $H_2C = O$, is made by the oxidation of methyl alcohol. The laboratory method (Fig. 65) is to draw air through *warm* methyl alcohol and then to draw the mixture of air and alcohol vapor over heated copper.

$$CH_3OH + O \longrightarrow H_2C=O + H_2O.$$

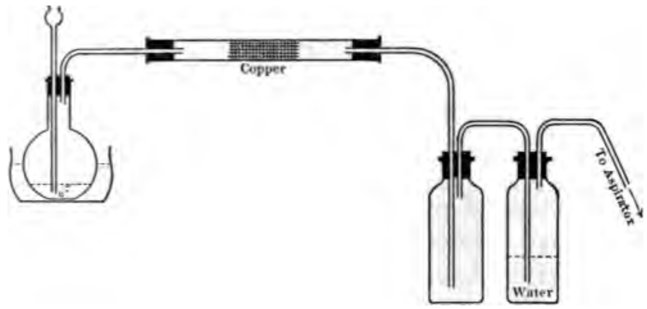


FIG. 65.

Formaldehyde is a colorless, irritating gas, very soluble in water. It is used as a disinfectant and preservative. *Formalin* is a 40% solution of formaldehyde.

Benzaldehyde, C_6H_5CHO (see table, § 478), is the oil of bitter almonds found in almonds and cherry kernels. It has a pleasant odor, boils at 179°, and is used as a flavor.

473. Halogen Derivatives. When marsh gas is treated with chlorine in diffused light, the products are *methyl chloride* (chlormethane) and hydrochloric acid.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl.$$

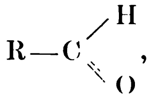
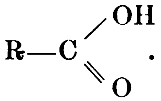
Under proper conditions the reaction may go further, giving *dichlormethane* (CH_2Cl_2), *trichlormethane*

($CHCl_3$), and even *tetrachlormethane* (CCl_4). Methyl chloride is gaseous at ordinary temperatures; the others are colorless liquids. Trichlormethane is **chloroform,** the anæsthetic (*cf.* § 337). It boils at 63° C.

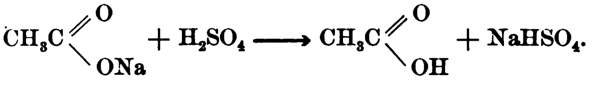
Chloroform is generally prepared by the action of bleaching powder upon alcohol or *acetone*, $(CH_3)_2CO$. It may also be made by the action of alkalies upon *chloral* (trichloracetaldehyde), CCl_3CHO.

Chloral is made by the action of chlorine upon alcohol; it is a liquid with a disagreeable odor. Like other aldehydes it combines with water, giving a *hydrate*. Chloral hydrate is often used by physicians to produce sleep.

Iodoform, CHI_3, is analogous to chloroform. It is a yellow solid, melting at 119°. It is used as a surgical dressing.

474. Organic Acids. — The organic acids are oxidation products of the corresponding aldehydes. While the general formula of aldehydes is  $R-C\begin{smallmatrix}/H\\ \backslash\backslash O\end{smallmatrix}$, that of acids is  $R-C\begin{smallmatrix}/OH\\ \backslash\backslash O\end{smallmatrix}$. The acids may be mono-, di-, tribasic, etc. The hydrogen of the CO.OH group is the *ionic* hydrogen (*cf.* § 351).

475. Acetic Acid. — Acetic acid (*cf.* §§ 98 and 201) is formed by the dry distillation of wood. The crude product (*pyroligneous acid*) is neutralized with lime or caustic soda. The resulting *acetate* is then purified and treated with concentrated sulphuric acid. The reaction is like that between chlorides, etc., and sulphuric acid (*cf.* § 157).



$$CH_3C\begin{matrix} /\!\!/O \\ \backslash ONa \end{matrix} + H_2SO_4 \longrightarrow CH_3C\begin{matrix} /\!\!/O \\ \backslash OH \end{matrix} + NaHSO_4.$$

sodium acetate *acetic acid*

If the acetate used is *anhydrous* the acid is obtained as a sharp-smelling liquid which solidifies to colorless crystals melting at about 17° C. (**glacial** acetic acid). It boils at 118° C. and mixes readily with water.

Sodium acetate, $NaC_2H_3O_2 + 3\ H_2O$, is a white solid used in making dyes. It loses its crystal water when heated.

Lead acetate, $PbC_2H_3O_2 + 3\ H_2O$ (*cf.* § 453), is used in making *lead chromate* (chrome yellow) and in dyeing (§ 449).

Impure *iron* and *aluminum* acetates are used as mordants in dyeing and in the printing of calico.

Verdigris, used for a blue paint, is basic copper acetate.

Paris green, an arseno-acetate, was mentioned in § 312.

476. Formic Acid, H_2CO_2. — Formic acid is found in stinging nettles and the bodies of red ants. It is prepared by heating *oxalic acid* with glycerine.

$$H_2C_2O_4 \longrightarrow H_2CO_2 + CO_2.$$

The anhydrous acid melts at 4° C. and boils at 100°. It produces blisters on the skin.

477. Vinegar. — As was stated in §§ 206 and 468, a ferment in yeast decomposes sugar, giving alcohol and carbon dioxide. If the dilute, impure alcohol (wine or cider) is allowed to stand in the air, a new fermenting agent ("mother of vinegar") oxidizes it to aldehyde and acetic acid. The dilute, impure acetic acid that results is *vinegar*.

On a large scale, vinegar is made in casks or vats filled with shavings and perforated so that air has free access. The shavings are "inoculated" by means of strong vinegar, and the dilute alcohol is allowed to trickle over them.

478. Other Acids. — Acetic and formic acids are the first members of an homologous series. The relation between some of these acids and the corresponding *hydrocarbons*, *alcohols*, and *aldehydes* is shown in the table. All except the last two are derived from marsh gas hydrocarbons.

HYDROCARBON.	ALCOHOL.	ALDEHYDE.	ACID.	
			FORMULA.	NAME.
CH_4	$H.CH_2OH$	$H.CHO$	$H.COOH$	Formic.
C_2H_6	CH_3CH_2OH	CH_3CHO	CH_3COOH	Acetic.
C_3H_8	$C_2H_5CH_2OH$	C_2H_5CHO	C_2H_5COOH	Propionic.
C_4H_{10}	$C_3H_7CH_2OH$	C_3H_7CHO	C_3H_7COOH	Butyric.
$C_{16}H_{34}$	$C_{15}H_{31}CH_2OH$	$C_{15}H_{31}CHO$	$C_{15}H_{31}COOH$	Palmitic.
$C_{18}H_{38}$	$C_{17}H_{35}CH_2OH$	$C_{17}H_{35}CHO$	$C_{17}H_{35}COOH$	Stearic.
$C_{18}H_{36}$			$C_{17}H_{33}COOH$	Oleic.
C_7H_8	$C_6H_5CH_2OH$	C_6H_5CHO	C_6H_5COOH	Benzoic.

Butyric acid is present in butter as the glycerine ester (*cf.* § 480) and is set free when the butter becomes rancid.

Benzoic acid is a white solid melting at 121° C. and subliming when heated.

Oxalic acid forms white, soluble crystals having the formula $H_2C_2O_4.2\ H_2O$. It acts as a reducing agent (*cf.* § 444). It is used in some of the processes of dyeing and photography, and to remove ink spots and rust from fabrics.

Lactic acid, $HC_3H_5O_3$, is produced by the fermentation of milk sugar (*cf.* § 483) and is, therefore, found in sour milk. It is present also in pickles and in the gastric juice. It is a thick, colorless liquid which decomposes when heated.

Tartaric acid, $H_2C_4H_4O_6$ (*cf.* § 98), forms large crystals. Its potassium hydrogen salt ("cream of tartar"; *cf.* § 206, *b*) is obtained from the walls of wine casks as a dark solid called "tartar" or "argol." From this the acid is prepared. For "tartar emetic" see § 318.

Malic acid, $H_2C_4H_4O_5$, occurs in fruits. It forms deliquescent crystals melting at 100°.

Citric acid, $H_3C_6H_5O_7 + H_2O$, forms crystals melting at 100°. It occurs in lemons, oranges, and other acid fruits. *Magnesium citrate* is a medicine.

479. Esters. — Alcohols react with acids (*cf.* § 467). producing water and *organic salts*, or **esters.** Thus acetic acid and alcohol produce ethyl acetate and water.

$$CH_3CO\overset{\prime}{O}H + HOC_2H_5 \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

The reaction is, however, **reversible:** water saponifies the ester (*cf.* § 366). To make the formation of the ester complete we remove the water from the "sphere of action" by means of concentrated sulphuric acid. Alkalies and dilute acids saponify the esters more rapidly than water. For ethyl acetate and sodium hydroxide the equation is:

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH.$$

Many esters present in fruits and flowers give to them a characteristic odor and taste. Artificial esters are often used instead of the natural flavors in the preparation of drinks, extracts, and perfumes. Thus *ethyl butyrate* has the odor and taste of pineapples; *amyl acetate*, that of bananas; *amyl valerianate*, that of apples.

480. Fats and Oils; Soaps. — The most important esters are the natural fats and oils, which consist essentially of the glycerine esters of *stearic*, *oleic*, and *palmitic* acids. These esters are called *stearin*, *olein*, and *palmitin*, respectively. The relative amount of olein present in the fats largely determines their fluidity, since olein is liquid at ordinary temperatures. The other two esters are solids. *Tallow* and *beef-suet* are largely stearin; *palm oil* is largely palmitin; *lard* and *olive oil* contain much olein; while *butter* is a mixture of several fats, — esters of palmitic, stearic, oleic, butyric, caproic, and capric acids. The last two have the formulas $C_5H_{11}COOH$ and $C_9H_{19}COOH$, respectively.

Soap. In making soap (*cf.* § 366) the alkali and the fat are heated in large kettles until the fat is saponified. The soap remains in solution until salt is added, which makes it rise to the top of the mixture. The salty solution is worked up for *glycerine*, while the soap is washed, perfumed, and colored, or "filled" with borax, sand, etc. It is then cut into bars and dried.

Hard soaps consist of the sodium salts, and soft soaps of the potassium salts of the organic acids. Palm oil, cocoanut oil, tallow and lard produce *white* soaps. In the *yellow* varieties these fats are mixed with rosin, cotton-seed oil, bone grease, etc. Olive oil is used in making "Castile" soap.

481. Amines. — Amines are composed of carbon, hydrogen, and nitrogen. They may be looked upon as *ammonia* with its hydrogen replaced by organic radicals (*cf.* § 467). *Methylamine* (CH_3NH_2) and *ethylamine* ($C_2H_5NH_2$) are gases much like ammonia. They are very soluble in water, and unite with acids, forming salts. The most important amine is **aniline** (phenylamine), $C_6H_5NH_2$. This is a colorless liquid made by reducing nitrobenzene.

$$C_6H_5NO_2 + 3\ H_2 \longrightarrow C_6H_5NH_2 + 2\ H_2O.$$

The nitrobenzene is reduced by adding to it tin (or iron) and hydrochloric acid. The resulting *aniline hydrochloride*, $C_6H_5NH_2.HCl$, is a white solid like ammonium chloride (*cf.* § 148). It is decomposed by caustic soda, liberating aniline.

Aniline is used in making aniline dyes and many other organic substances.

482. Alkaloids. — Alkaloids are nitrogenous substances occurring in plants and often used in medicine because of their physiological effect. Chemically they resemble ammonia: they unite with acids to form salts, and their aqueous solutions are alkaline.

Quinine, $C_{20}H_{24}N_2O_2$, is found in the bark of cinchona trees, and is used to reduce fevers.

Morphine, $C_{17}H_{19}NO_3$, which occurs with other alkaloids in *opium*, is used to deaden pain. Opium is made by evaporating the sap of unripe poppies. *Paregoric* and *laudanum* are prepared from it.

Strychnine ($C_{21}H_{22}N_2O_2$) and *brucine* ($C_{23}H_{26}N_2O_4$) occur in *nux vomica.*

Cocaine is found in cocoa leaves. Its salt, $C_{17}H_{21}NO_4.HCl$, is used by dentists and surgeons as a local anæsthetic.

Theïne (or caffeïne), $C_8H_{10}N_4O_2 + H_2O$, is the active constituent of tea and coffee.

Nicotine, $C_{10}H_{14}N_2$, occurs in tobacco as the *malate.*

483. Sugars. — Sugars, starch, and cellulose are the most important substances of the class of compounds known as *carbohydrates.* The most common sugar is *cane sugar*, which is made from sugar cane and from beets. Its formula is $C_{12}H_{22}O_{11}$. Isomeric with it (*cf.* § 262) are *maltose* (malt sugar) and *lactose* (sugar of milk). When cane sugar is exposed to certain ferments, or heated with dilute acids, it is *hydrolyzed* according to the equation:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\textit{glucose}}{C_6H_{12}O_6} + \underset{\textit{fructose}}{C_6H_{12}O_6}.$$

Maltose decomposes according to a similar equation, but only glucose is formed. Lactose gives glucose and *galactose.* All sugars contain (OH) groups, like alcohols (*cf.* §§ 467 and 470).

Milk sugar is not so sweet as cane sugar. It forms hard, white crystals, and is used for prepared foods and homeopathic pellets. The lactic acid ferment decomposes it (*cf.* § 478).

Cane sugar melts at about 160° C. At about 200° it forms a brown substance called *caramel*, which is used as a coloring for foods and liquors.

484. Manufacture of Cane Sugar. — Cane sugar, or *sucrose*, is prepared from the cane by crushing it and boiling the juice with lime. The lime clarifies the juice. After filtration the sugar solution is evaporated until a cooled sample begins to crystallize. The evaporation is then continued in "vacuum pans," so that the water distills off at a temperature below that at which it would boil under atmospheric pressure (*cf.* § 290). The crystals of sugar are separated from the liquid (molasses) by rotating the mixture in funnel shaped sieves through which only the molasses can escape. *Raw* or *brown sugar* is thus obtained. The preparation of sugar from beets takes place in a similar way.

The *second* operation is the **refining** of raw sugar. In this process the raw sugar is dissolved in hot water, the solution is stirred by blowing air through it, and coagulating substances are added to collect the impurities. Animal charcoal is used to make the solution colorless (*cf.* § 201). The resulting syrup is then concentrated in vacuum pans and left in tanks until it crystallizes. Finally the crystals of sugar are separated from the adhering syrup in centrifugal apparatus and dried carefully for the market.

485. Glucose and Fructose. — *Glucose*, $C_6H_{12}O_6$, — also called dextrose and grape sugar, — is a white, crystalline solid less sweet than cane sugar. It melts at about 150° C. Glucose is found in grapes, and, therefore, in raisins. It occurs in the seeds, roots, leaves, and blossoms of plants, and is formed by the hydrolysis of sucrose, maltose, and lactose. Glucose reduces alkaline copper solution (Fehling's solution) giving *cuprous oxide* (*cf.* § 410).

Fructose (levulose or fruit sugar) is isomeric with glucose. It is a white solid, melting at 107°–109°, and is almost as sweet as sucrose. Both glucose and fructose are fermentable.

Commercial glucose is made by heating starch with dilute sulphuric acid. This hydrolyzes the starch, giving several intermediate products, and finally glucose. The part that crystallizes out is called "grape sugar," while the colorless syrup is called "glucose" or "mixing syrup." "Glucose" is used in the preparation of jellies, candy, and syrups.

486. Glucosides. — While in cane sugar and milk sugar glucose is combined with fructose and galactose, respectively, in many other natural compounds it is combined with benzene derivatives. These are called *glucosides.* Amygdalin, the tannins, and indican are examples.

Amygdalin, $C_{20}H_{27}NO_{11}$, is found in bitter almonds and in the kernels of many fruits, such as peaches, cherries, and plums. The ferment *emulsin* and dilute acids decompose it into glucose, prussic acid, and benzaldehyde.

$$C_{20}H_{27}NO_{11} + 2\ H_2O \longrightarrow 2\ C_6H_{12}O_6 + HCN + C_6H_5CHO.$$

Tannins are found in the bark and leaves of many plants. The chief sources are hemlock and oak bark, but they occur also in tea, sumach, gall nuts, etc. Not all of the tannins are glucosides.

484. Manufacture of
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with dilute acids, it breaks down into
the well known dyestuff. Indigo has
N_2O_2. It is now prepared synthetically in

Starch.—Starch is found in grains, potatoes, It is made from maize and potatoes by them to powdered form, adding water, and ting the starch, which is practically insoluble, from the gluten, oil, and cellulose with which it is mixed. Starch consists of small grains of varied appearance. Hot water causes the grains to swell and burst. The resulting starch paste dissolves (*cf.* Experiment XLIV, *f*). Starch is used in foods, in making cloth, paper, and glucose, and for "starching" clothes. The formula of starch is $(C_6H_{10}O_5)_n + H_2O$. The value of *n* is not known.

Dextrin is formed from starch by the action of dilute acids. The sticky solution (impure dextrin) is used for mucilage.

Bread is made from flour by the fermenting action of yeast. Wheat flour consists largely of starch (about 70%) with about 15% each of water and gluten, besides small amounts of salts

When flour, water (or milk), and yeast are a dough and set in a warm place, the yeast changes present as such, or produced from the starch) into and carbon dioxide, and the bread "rises." In baking, yeast is killed; water, carbon dioxide, and alcohol escape, and the starch on the outside of the bread is partly changed to dextrin, forming the crust.

488. Cellulose $(C_6H_{10}O_5)_x$. — Cellulose is the basis of vegetable tissue, since it forms the walls of plant cells. Cotton, linen, and paper are almost wholly cellulose. Swedish filter paper is a purified form. Cellulose is an amorphous, white substance insoluble in most solvents. When treated with concentrated sulphuric acid and then with water it breaks down into glucose. Like alcohols, cellulose reacts with acids to form *esters*. The nitric acid esters were mentioned in § 165. *Collodion* is nitrocellulose dissolved in alcohol and ether. When the solvent evaporates it leaves a thin film of nitrocellulose. Collodion can thus be used to protect wounds and to attach silver salts to photographic plates (*cf.* § 417).

Paper is made from rags, wood, or straw. The process consists of several stages:

1. Reducing the raw material to pulp and drying and pressing the pulp.
2. Mixing the pulp with clay or gypsum ("filling") to give the paper a close texture.
3. "Sizing" pulp that is to be converted into printing or writing paper, so that the ink will not spread. Gelatin, rosin, or alum is used for this.

4. Polishing the paper by passing it between rollers.

The conversion of wood into pulp is accomplished by first reducing it to chips and then heating the chips, under pressure, with sodium hydroxide or calcium acid sulphite ("bisulphite"; *cf.* § 193). Newspaper and wrapping paper are generally unsized; blotting and tissue papers are neither sized nor filled.

489. Phenol and its Derivatives. — Phenol, or *hydroxybenzene*, C_6H_5OH, is found in coal tar (*cf.* § 223). It is a white, crystalline, low-melting solid, which burns the skin and is poisonous. Its aqueous solution is used as a disinfectant. Phenol reacts with alkalies to give salts; it is sometimes called *carbolic acid.*

Salicylic Acid. When the sodium salt of phenol is treated with carbon dioxide at 120°, under pressure, the two unite to give *sodium salicylate*, $C_6H_4OH.COONa$. This is used in medicine. Salicylic acid is a white solid melting at 156° and used as a preservative. Its *methyl ester*, $C_6H_4OHCOOCH_3$, is present in oil of wintergreen.

Picric Acid, or trinitrophenol, $C_6H_2(NO_2)_3OH$, is made from phenol and fuming nitric acid. It is a yellow, soluble solid used as a dye. Some of the picrates are used in making explosives.

Hydroquinone, $C_6H_4(OH)_2$, and **pyrogallic acid,** $C_6H_3(OH)_3$, are di- and tri-hydroxybenzene, respectively. They are soluble, white solids. Both are reducing agents and are used as developers in photography (*cf.* § 417). Pyrogallic acid (also called *pyrogallol*) is used to absorb uncombined oxygen in gas analysis.

LABORATORY DIRECTIONS.

(*For the Student.*)

1. Provide yourself with an apron and a pair of sleeves (rubber is the best material for these); also with soap and towel, and a white cloth about a yard square. The cloth is to be used for wiping apparatus.

2. Work by yourself; and give *your own* descriptions, observations, and calculations, not those of *another*.

3. Record *at once* all the observations you make in connection with an experiment. See that your notes contain the answer to every question, direct or implied, that occurs in the laboratory exercise. Write neatly and distinctly. If the notes of two experiments occur on the same page, separate them by at least two centimeters of space.

4. Have a place for everything. Throw away nothing until you are sure you are through with it. Throw nothing but liquids into the sink. Put other waste materials into the proper receptacle.

5. If an experiment is unsatisfactory, repeat it until you are successful; but *first* learn the probable cause of your error.

6. When you enter the laboratory, examine your table, and see that everything has been left as it should be by the persons who share the table with you. If anything is wrong, report the fact *at once* to the instructor.

When you leave, see that the water and the gas are turned off, and that everything on your table is in good order.

LABORATORY EXERCISES.

EXPERIMENT I.

THE BUNSEN BURNER.

Apparatus. — Bunsen burner, test tube, test-tube holder (see note below).

Materials. — Matches, water.

a. Examine carefully the Bunsen burner on your desk. Take it apart, and draw a sketch of each part.

b. Put the burner together, close the holes at the base, and connect with gas supply.

To light the burner, turn on the gas and then hold a lighted match near the side of the burner and about one-half a centimeter below its mouth. Note the character of the flame; is it luminous or not? Now open the holes carefully until the luminous region has just disappeared. This is the "Bunsen" flame. For most work it should be 7 to 10 centimeters (3 to 4 inches) high. The holes of the burner should be open far enough to prevent a deposit of soot upon the object heated, but not far enough to cause the flame to make a noise.

c. Introduce quickly into the center of the Bunsen flame, one-half a centimeter above the burner, the head end of a match. Result? Is the gas in this region burning?

To heat an object effectively, place it higher up in the flame; the best place is just above the apex of the dark, inner cone of unburned gas. Locate this region.

d. Put 5 c.c. water into a test tube, and make a note of the height of the column of water in centimeters. Whenever you are asked to take 2, 5, 10, etc., cubic centimeters of anything, refer to this experiment, and use the length of the column just measured as your *unit.*

e. Heat the water in the test tube to boiling. To do this properly have the outside of the tube *dry;* hold the tube in the holder, and incline the tube at an angle of about 45° to the table top. Then introduce the bottom of the tube into the effective region (cf. *c*) of the flame. *Heat only the part of the tube containing the liquid;* if the flame strikes the glass above the liquid level, the tube may crack. *Do not hold the tube still,* but move it gently in the flame. When boiling begins, raise the tube a little above the flame, — always keeping it inclined, — so that the water may not "boil over."

f. These directions are general, and will apply whenever you heat liquids in test tubes.

Note. — A very convenient test-tube holder can be made by folding a piece of writing paper twice, so as to produce a strip about 1 cm. wide and 10 to 15 cm. long. This is placed about the tube like a holder. The free ends are held together close to the tube.

EXPERIMENT II.

CUTTING AND BENDING GLASS TUBING.

Apparatus. — Bunsen burner, "wing-top" or illuminating gas burner, file.

Materials. — Piece of soft glass tubing more than 15 cm. long.

a. Cut off a piece of glass tubing 15 cm. long. To do this, make on the tubing a file mark in a plane perpendicular to the length of the tubing; grasp the tube in both hands, and place the thumb nails together opposite the scratch. By *pushing* gently *with the thumbs* and at the same time *pulling with the hands* you will succeed in breaking the tubing so that the ends are fairly regular.

b. Round off both ends of the 15 cm. tube by turning them about in the proper region of the Bunsen flame until the edges become red hot. Let the ends cool.

c. Bend the 15 cm. tube at its middle into the form of a right angle. For this purpose use a *flat* Bunsen flame — produced by a "wing-top" attachment — or a flat illuminating flame.

Take the tube in both hands, one at each end, and hold its central part *lengthwise with* and *over* the flat flame. At the same time twirl the tube between thumbs and forefingers. Then lower the tube — keep turning it — into the upper part of the flame, and heat until you find that the glass is fairly soft. Then bend *gently* to a right angle.

d. If you used the Bunsen flame, *anneal* the glass at the bend by closing the holes of the burner and allowing the hot glass to cool first in the *smoky* flame. When the bend is covered with soot, support it so that it will not touch a cold object. When the tube is cold, wipe off the soot.

EXPERIMENT III.

EFFECT OF HEAT UPON "RED PRECIPITATE."

Apparatus. — Small ignition tube of hard glass, rubber connecting tube, delivery tube, pneumatic trough, test tube, ring stand, clamp.

Materials. — Pine splinter, red precipitate.

a. In a small tube of hard glass sealed at one end and about 10 cm. long — "ignition tube" — place a layer of red precipitate *not more than* one-half a centimeter thick.

In a basin containing water, invert a test tube of water. See that no air bubbles remain in the test tube. Vessels for holding water over which gases are collected are called "pneumatic troughs."

Attach to the ignition tube by means of a piece of rubber tubing a delivery tube long enough to reach to the bottom of the pneumatic trough. Support the ignition and delivery tubes so that the closed end of the ignition tube is only a little lower than its other end, and so that the red precipitate may be heated in the hot portion of the Bunsen flame.

b. Begin to heat slowly, keeping the flame in motion. Note any change in color of the red precipitate. Afterward heat *strongly* with a steady flame until all of the powder disappears. Collect *over water* anything that escapes from the delivery tube by allowing it to displace the water of the test tube. When the operation is over, *remove the delivery tube from the water before removing the flame.* Why?

c. Cover the mouth of the test tube under water with the thumb, remove tube from water, invert, and introduce a pine splinter with a *spark* on the end of it. Result? Is the gas in the test tube *air?*

d. When the ignition tube is cool, invert it and strike its open end sharply against the table. Result? What substance is this? On what part of the tube did it collect? Why?

e. If by a *chemical change* we mean one in which at least *one* new substance is formed, would you call this a chemical change, or not?

EXPERIMENT IV.

SOLUTION, FILTRATION, AND EVAPORATION.

Apparatus. — Glass rod 15 cm. long (unfinished), file, two beakers of about 50 c.c. capacity, ring stand, wire gauze, funnel, funnel support (small ring of ring stand), evaporating dish.

Materials. — Coarse salt, filter paper.

a. Make a glass stirring rod 15 cm. long, cutting off a piece from a larger one, just as in Experiment II, *a.* Round off both ends in the flame.

b. Put into a beaker about 20 c.c. cold water, add 5 grams salt, and heat the beaker over the flame until its contents boil. Before heating the beaker see that it is *dry* on the outside, then place it upon a wire gauze supported on the ring stand. Move the flame about under the gauze until the beaker has become *warm;* then put the burner under the center of the beaker. The height of the gauze above the burner should be so great that the bottom of the beaker may be a little above the apex of the dark inner region of the flame.

Note. — *Always follow these directions* when you are heating a beaker, an evaporating dish, or a flask, unless there is some special reason for not doing so. What becomes of the salt? Of the dirt?

c. Next, *filter* the solution. You need a funnel, a support (see above), a filter, the glass rod made in *a*, and a second beaker.

Fold the circular filter twice in lines at right angles to each other. Press the folded edges between thumb and forefinger, but *not* between the nails. Open the filter so that it shall form an inverted cone which just *fits* the funnel. One-half of the conical surface is made up of three of the quarters into which the paper was folded; the remaining quarter of the paper makes up the other half of the cone.

d. Hold the filter in place in the funnel, and wet it completely; it should adhere everywhere to the inner surface of the funnel, and its point should extend a little into the stem of the funnel.

Pour the salt solution down the glass rod to the filter.

The glass rod should touch the lip of the beaker; and the stem of the funnel should touch the side of the beaker beneath it.

Always follow these directions in filtering an insoluble solid from a solution.

e. Does anything remain on the filter? We call it the *residue.* What passes through is the *filtrate.*

A substance which remains *mixed* with a liquid, but not dissolved in it, is said to be "suspended in," or "held in suspension by" the liquid.

A *suspended* substance becomes, after filtration, a *residue.*

f. Pour the filtrate of *c* into an evaporating dish, and heat (for precautions, cf. *b*) over the flame. Boil off the water until a solid begins to separate out; then set the dish aside until it is cold, or until the next laboratory period. What is the solid obtained?

Is this separation of the salt from the dirt a physical or a chemical operation?

EXPERIMENT V.

HYDROGEN.

Apparatus. — Generating flask, or bottle of 250 c.c. capacity, two-holed stopper, funnel tube, right-angled tube, rubber connector, delivery tube, pneumatic trough, squares of glass or of cardboard, two or more wide-mouth collecting bottles (250 c.c.).

Materials. — Zinc, dilute sulphuric acid (one part by volume of acid to four volumes of water), pine splinter, cupric sulphate solution.

a. To a 250 c.c. flask containing enough zinc to cover the bottom fit a two-holed stopper. One of the holes is for a funnel tube reaching to within one-half a centimeter of the bottom of the flask when the stopper is in place; the other hole contains a bent tube attached by a rubber connector to a delivery tube. The delivery tube reaches to a pneumatic trough containing two bottles filled with water and inverted. The level of the water in the trough should be about two

What two *new* products resulted from the action of zinc and dilute sulphuric acid?

EXPERIMENT VI.

EQUIVALENT OF MAGNESIUM.

Apparatus. — Balances, pneumatic trough, wide-mouth bottle (250 c.c.), graduated jar, glass or cardboard cover.

Materials. — Magnesium wire, dilute (5%) sulphuric acid.

a. In a pneumatic trough containing water to the depth of about 3 cm. place a piece of magnesium wire the exact weight of which is known. There should be not more than 0.2 gram.

b. Get the exact capacity in cubic centimeters of a wide-mouth bottle by *filling* it with water and pouring the water into a graduated vessel. The bottle should hold at least 250 c.c.

c. Fill the bottle with 5% sulphuric acid, and invert it in the pneumatic trough as far from the magnesium as possible. See that the bottle is free from air bubbles.

Now slide the mouth of the bottle, under water, over the magnesium. Result?

d. When all the metal has disappeared let the collected gas cool to room temperature for 5 minutes. Then add water of room temperature to the bowl, *if necessary*, so that the level of water in bottle and bowl shall be the same. Why?

Protect the bottle from the heat of the hand by grasping it with a towel; then slip under its mouth a glass or cardboard cover, and invert *quickly*, so as to lose none of the water in the bottle.

Bring a flame to the mouth of the bottle *at once*. Result?

The gas is *hydrogen*. The other product of the reaction is magnesium sulphate; it remains in solution.

e. Get the volume of the water remaining in the bottle by means of the graduated vessel. Then obtain *by difference* the volume of hydrogen.

To get the weight of the hydrogen multiply its volume in cubic centimeters by the weight of 1 c.c. Get the weight of 1 c.c. under the conditions of the experiment from the teacher. What is your result?

f. Solve the following proportion for x : weight of magnesium : weight of hydrogen :: x : 1. Result? x will be the **equivalent** of magnesium, i. e., *the number of grams of magnesium required to liberate 1 gram of hydrogen* (in this case from dilute sulphuric acid).

EXPERIMENT VII.

OXYGEN.

Apparatus.—Mortar and pestle (?), test tubes, ring stand and clamp, one-holed stopper, delivery tube, pneumatic trough, 3 collecting bottles, glass or cardboard cover, deflagration spoon.

Materials.—Powdered potassium chlorate and manganese dioxide, pine splinter, sulphur, iron wire (picture cord) at least 15 cm. long.

a. On a *clean* piece of writing paper mix carefully 5 grams powdered potassium chlorate with 5 grams powdered manganese dioxide. If the substances are not found in powdered form in the laboratory, grind them *separately*, in *clean* mortars, before mixing.

b. Before you use the whole mixture, test the quality of a sample (1 c.c.) by heating it gently in an *open* test tube. If there is any evidence of *violent combustion*, or if *large* sparks appear, reject the mixture, and make a fresh one. A few *small* sparks indicate only traces of dust, etc.

c. If the mixture is satisfactory, put it into a test tube supported by a clamp attached to a ring stand. The test tube is then fitted with a one-holed stopper and a delivery tube reaching under water in a pneumatic trough.

Have 3 bottles filled with water and inverted in the trough.

d. Heat the test tube *gently* from the top of the mixture *downward.* Regulate the flame so as to keep the evolution of gas *steady*, *but not violent. Keep the flame in motion*, so as not to soften the glass.

When the collecting bottles are full, *first* take the delivery tube out of the water, and *then* remove the flame. Why this precaution?

The gas is **oxygen.**

e. Into one bottle of the gas put a glowing splinter as in Experiment III, *b*. Result? Gradually lower the splinter into the bottle until combustion stops. What becomes of the splinter? Of the oxygen?

To the contents of the bottle add 5 c.c. calcium hydroxide solution (lime-water), cover with the hand, and shake vigorously. Result?

f. Note the odor of the gas in the second bottle. Then put into the bottle a deflagrating spoon containing burning sulphur. Light the sulphur by holding the spoon in a flame.

Have a cardboard cover with a small hole for the handle of the deflagrating spoon, and keep the bottle covered until combustion stops. Results?

What becomes of the sulphur? Of the oxygen? Note the odor of the gas now in the bottle. Does this gas support the combustion of a splinter? Try it.

g. Have the third bottle of oxygen covered and set upright on the table. Draw aside the cover for a moment while you pour in 5 c.c. sand; then replace the cover.

Melt the sulphur left in the deflagrating spoon, and dip into it one end of a piece of iron picture cord. Light the sulphur tip, and *at once* hold the iron wire in the bottle of oxygen. Result? Keep the wire in the gas until action ceases. Describe the product. Why was the iron tipped with sulphur?

EXPERIMENT VIII.

KINDLING TEMPERATURE.

Apparatus.—Wire gauze at least 15 cm. square, Bunsen burner, tongs.

Material.—Matches.

a. Hold the wire gauze, by means of your tongs, 7 cm. *above* the Bunsen burner. Have the holes of the burner *open* as for the Bunsen flame. Now turn on the gas and bring a burning match *from above* down to the center of the gauze. Result?

Why does not the gas *below* the gauze take fire? Is there gas below the gauze? Prove it.

b. Let the gauze cool; and then bring it down upon the Bunsen flame until the gauze is 6 to 7 cm. above the top of the burner. Result? Hold the gauze in place until it becomes red hot. Result? Explain.

EXPERIMENT IX.

ACTION OF SODIUM UPON WATER.

Apparatus. — Tongs, evaporating dish.

Materials. — Sodium, water, blue and red litmus paper, solid sodium hydroxide.

Caution. — Do not handle sodium with **wet hands,** or with **wet forceps.** Do not put sodium into the waste jar. **On no account** leave any sodium on or about your desk or in your locker. Sodium is usually kept under kerosene.

a. What is the appearance of a freshly cut surface of sodium? Is sodium hard or soft? Heavy or light?

b. Hold a piece of sodium having a volume not greater than 8 to 10 c.mm. *at arm's length* by means of iron tongs or forceps, and drop it upon water in a small evaporating dish. Result?

Apply a lighted match — *hold it at arm's length* — to the sodium while it is acting on the water. Result?

c. After action has ceased, wet your fingers with the solution, and rub them together. Result? If you get no decided result, add a second piece of sodium (**dry hands**) of the same size as the first, and repeat.

d. Test the action of a drop of the solution upon a piece of blue litmus paper. Upon red litmus paper. Results?

e. Add a *small* piece (same size as sodium used) of sodium hydroxide to 5 c.c. water. Results? Test solution with the fingers and with litmus. Results? Compare results with those in *d.* Conclusion.

EXPERIMENT X.

WATER OF CRYSTALLIZATION.

Apparatus. — Test tubes, iron saucer (sand bath).

Materials. — Crystals of zinc sulphate, of potash alum (potassium aluminum sulphate), and of cupric sulphate.

a. Place a few crystals of zinc sulphate in a *dry* test tube, and warm *gently.* Results? Is there evidence of water? Where?

b. Repeat *a*, using a crystal of potash alum. Results?

c. Note the taste of another crystal of potash alum; then heat it *strongly* in an iron dish until no further change occurs. Results?

When the ignited alum is *cold*, taste it. Result? Place it in 5 c.c. water in a test tube, and boil carefully for five minutes. When the water is cool, taste it. Result?

Assuming that heat simply drove off crystal-water from the alum, upon what does the taste of crystalline alum seem to depend?

d. Heat a crystal of copper sulphate (blue vitriol) strongly in an iron dish. Result? When the residue is cold, add a few drops of water to it. Result? Explain.

EXPERIMENT XI.

EFFLORESCENCE.

Apparatus. — Evaporating dish.

Materials. — Crystallized sodium carbonate and sodium sulphate (Glauber's salt).

a. Expose a crystal or two of sodium carbonate to the air for at least twenty-four hours. Result?

b. Carefully weigh your evaporating dish, and then weigh into it *accurately* about 5 grams Glauber's salt (sodium sulphate *plus* crystal-water). Let stand for at least twenty-four hours, and weigh again. Result? What change is there in the appearance of the substance? Record your results thus: —

Grams.

(1) Weight of evaporating dish + Glauber's salt =

(2) Weight of evaporating dish alone = ______

(3) ∴ Weight of Glauber's salt taken =

(4) Weight of evaporating dish + residue = ______

∴ gain or loss of water [subtract (4) from (1)] = ______

EXPERIMENT XII.

DELIQUESCENCE.

Apparatus. — Small beaker, evaporating dish *or* watch glass.

Materials. — Solid potassium hydroxide, *granular* calcium chloride.

a. In a small beaker place a piece of potassium hydroxide, and leave it exposed to the air at least an hour. Result?

b. Weigh an evaporating dish or a watch glass carefully, and then weigh into it *accurately* about 5 grams anhydrous calcium chloride. Let stand at least twenty-four hours, and weigh again. Results? Record the weighings as in Experiment XI, *b.*

EXPERIMENT XIII.

EFFECT OF TEMPERATURE ON SOLUTION.

CRYSTALLIZATION.

Apparatus. — Beaker (50 c.c.), stirring rod.

Materials. — Potash alum, crystallized cupric sulphate (blue vitriol).

a. Put 20 c.c. water into a beaker, add 10 grams powdered alum, and stir two minutes with the stirring rod. Does all the alum dissolve?

b. Heat the beaker carefully on the wire gauze, stirring the contents. Result? Conclusion.

c. Set the beaker with the hot solution in cold water, and stir rapidly until solution cools. Result?

d. Dry the outside of the beaker, and heat again as in *b.* Result? Let the solution stand undisturbed until it is cold. Result? Compare with *c*, and account for the difference.

e. Repeat *a*, *b*, *c*, and *d*, with 20 c.c. water and 15 grams powdered blue vitriol. Results?

EXPERIMENT XIV.

PRECIPITATION.

Apparatus. — Test tubes.

Materials. — Solutions of lead nitrate, potassium chromate, barium chloride, and calcium sulphate. Dilute sulphuric acid; alcohol.

a. To 5 c.c. of lead nitrate solution in a test tube add an equal volume of potassium chromate solution. Result? Let tube stand ten to fifteen minutes. Result? The precipitate is *lead chromate.*

b. Repeat *a*, putting together hot barium chloride solution and dilute sulphuric acid. Result after ten to fifteen minutes? The precipitate is *barium sulphate.*

c. To 2 c.c. calcium sulphate solution add an equal volume of alcohol. Result? The precipitate is *calcium sulphate.*

Note. — The insoluble solids formed in *a* and *b* are not the only products of these reactions; the other products are, however, soluble.

EXPERIMENT XV.

CONSTANT PROPORTIONS.

Apparatus. — Evaporating dishes, beaker, balances, watch glass.

Materials. — Crystallized sodium carbonate, dilute hydrochloric acid (1 volume concentrated acid to 1 volume water).

a. Weigh your evaporating dish carefully, and then weig[illegible] into it *accurately* about 5 grams sodium carbonate crystal[illegible]. Transfer the sodium carbonate *without loss* to a beaker cov[illegible] ered with a watch glass; then add the dilute hydrochloric acid a little at a time. When adding acid draw the watch glass a little to one side; at other times let it cover the beaker.

b. The *effervescence* (foaming) is due to the escape of carbon dioxide gas. When all the crystals have dissolved, add a drop or two more of the acid, to be sure no sodium carbonate remains; then pour the solution into the weighed evaporating dish. With 5 c.c. water, wash what has spattered on the watch glass into the beaker, and with this water rinse what adheres to the beaker into the evaporating dish. Rinse the beaker with 5 c.c. more water, and add the rinsings to the evaporating dish.

c. Evaporate the solution to *dryness*, on a water bath or a steam bath, if possible; otherwise, on a wire gauze. If you use wire gauze take great care to avoid spattering either the solution or the solid which remains after the water has boiled away. If considerable spattering begins, remove the flame for a moment and let the dish cool; then apply the flame again *gently*. *Keep flame in constant motion at the end of the process.*

When the solid in the dish is perfectly dry, let the dish cool to the temperature of the room. Then weigh it *accurately*.

d. Record your results thus: —

	Grams.
Weight of evaporating dish + sodium carbonate =	
Weight of evaporating dish alone =	——
∴ Weight of sodium carbonate used =	
Weight of evaporating dish + sodium chloride =	
Weight of evaporating dish alone =	——
∴ Weight of sodium chloride formed =	

Get the simplest ratio between the amount of sodium carbonate taken and that of sodium chloride obtained as follows: Weight of sodium carbonate : weight of sodium chloride :: 1 : x. Calculate the value of x to two decimal places. $x = ?$

e. Repeat the preceding operations, weighing out *accurately* about 8 grams sodium carbonate crystals. If the volume of the solution is too great to go into the evaporating dish *all at once*, evaporate part of the water and then add the remainder of the solution. ***Be sure to rinse.***

Calculate the ratio between sodium carbonate and sodium chloride as before. Compare the ratios. Conclusion?

EXPERIMENT XVI.

CHLORINE.

Caution. — *Avoid inhaling much chlorine.* If you have inhaled it, smell ammonia cautiously. If the gas gets into the room, sprinkle a few drops of ammonia water upon your table.

Apparatus. — 100 c.c. flask, ring stand, wire gauze, one-holed stopper, two right-angled tubes (one with long arm), rubber connector, collecting bottle, test tubes, perforated cardboard cover.

Materials. — Manganese dioxide (in lumps), concentrated hydrochloric acid, white paper, red cheese cloth, litmus solution, indigo solution, potassium chlorate, ink, printed paper.

a. Support a 100 c.c. flask on a wire gauze in a ring stand. The flask is provided with a one-holed stopper and a delivery tube bent twice at right angles. The double bend is produced by joining two right-angle tubes by means of a rubber connector. The second right-angle tube is turned down; its end should be 2 to 3 cm. above the table.

b. Put into the flask 5 grams manganese dioxide in small lumps (so-called *crystalline* manganese dioxide), add 20 c.c. concentrated hydrochloric acid, and attach stopper and delivery tube.

Warm the flask *gently*, and fill a dry bottle, turned mouth up, with the resulting *chlorine* gas. While the bottle is being filled keep it covered with a piece of cardboard; the cardboard has a hole for the delivery tube. You may know when the bottle is full by the rise of chlorine to the top; white paper held behind the bottle will help you.

c. Stopper the bottle when it is full, and fill two dry test tubes with the gas. Then pass the gas for five minutes into 15 c.c. *cold* water in a test tube. This gives *chlorine water.*

When you are through, disconnect the apparatus *at once*, and wash the remaining manganese dioxide twice with water.

d. What is the color of the gas? Apply a lighted match to a test tube of it. Does the gas burn? Support combustion?

e. Put into the bottle of the gas a small piece (2 cm. square) of *dry* red cheese cloth, a *wet* piece of the same, a piece of paper containing print, and a paper with ink marks. Leave 10 to 15 minutes. Results?

f. Put 5 c.c. of the solution of chlorine made in *c* upon 1 sq. cm. of the colored cloth in a test tube. Upon paper with both print and ink marks on it. Results? What seems to be necessary in order that chlorine may bleach?

g. Into a test tube of the gas pour 5 c.c. cold water, close the mouth of the test tube tightly with the thumb, and shake *vigorously*. Remove thumb under water. Result? Explain.

h. To 1 c.c. dilute litmus solution, add chlorine water until you get a decided change. Explain result. Repeat, using indigo solution instead of litmus. Result?

i. An easy way to make a solution of chlorine is to treat about 1 gram of potassium chlorate with 5 c.c. concentrated hydrochloric acid. If action is *slow*, warm *gently*. When the effervescence is rapid, add 10 c.c. cold water.

EXPERIMENT XVII.

HYDROCHLORIC ACID.

Apparatus. — Same as in Experiment XVI.

Materials. — Sodium chloride, concentrated sulphuric acid, red and blue litmus paper, iron filings, silver nitrate solution, ammonium hydroxide solution, dilute hydrochloric acid, sodium chloride solution, calcium chloride solution.

a. Into a 100 c.c. flask with stopper and delivery tube as in Experiment XVI, put 5 to 7 c.c. water, and add *carefully* 20 c.c. concentrated sulphuric acid. Result?

Caution. — In diluting sulphuric acid always pour the acid *into the water*.

b. Cool the diluted acid by holding the flask in a stream of running water. When the acid is cold, put into it about 15 grams sodium chloride.

c. Attach the stopper and the delivery tube, and place the flask on the wire gauze of a ring stand. Warm carefully with a small flame, and fill a *dry* bottle with the gas, — it is *hydrochloric acid gas,* — as in Experiment XVI, *b.*

You may know that the bottle is full when white fumes escape about the cardboard which covers the collecting bottle.

Fill, also, a dry test tube, and stopper both vessels.

d. Test the gas at the end of the delivery tube with strips of moistened red and blue litmus paper. Results?

Blow your breath against the stream of gas. Result? Explain.

e. Now let the end of the delivery tube come *just to the surface* of 5 c.c. water in a test tube. Note the appearance of the water below the delivery tube. While the gas is coming off regularly, raise the test tube so that the end of the delivery tube is about 2 cm. below the water level. Do gas bubbles pass *through* the water? Why? Lower the test tube again until the delivery tube is at the surface, and let the gas run into the water five minutes. Is there any change in temperature?

Finally remove the delivery tube from the water and extinguish the flame. Save the liquid.

Lower the wire gauze so as to let the flask cool out of contact with the gauze..

f. Open the test tube of gas under water. Result? Explain.

g. Hold a burning match in the bottle of gas. Does the gas burn? Does it support combustion?

h. Test the liquid obtained in *e* with red and blue litmus. Compare results with those given by the gas. Add a drop of the liquid to 2 c.c. water, and taste a drop held on a stirring rod. Result?

i. Pour some of the liquid of *e* upon 1 c.c. iron filings in a test tube. Result? Does the gas burn?

The equation is: $Fe + 2\ HCl \longrightarrow FeCl_2 + ?$

j. Add a few drops of the liquid of *e* to 1 c.c. silver nitrate solution in a test tube. Result? The white precipitate is *silver chloride*, AgCl.

The equation is:

$$\underset{\text{silver nitrate}}{AgNO_3} + \underset{\text{hydrochloric acid}}{HCl} = AgCl + \underset{\text{nitric acid}}{HNO_3}.$$

To the precipitate add an excess of ammonium hydroxide solution, close the test tube with the thumb, and shake vigorously. Result?

k. Repeat *j*, using sodium chloride solution in place of hydrochloric acid. Result?

l. Repeat *j* again with calcium chloride solution in place of the acid. Results? Conclusion?

m. Note the white solid which separates when the flask becomes cool. It is chiefly sodium hydrogen sulphate, $NaHSO_4$.

The reaction between sodium chloride and sulphuric acid takes place according to the equation,—

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl.$$

EXPERIMENT XVIII.

PROPERTIES OF ACIDS.

Apparatus.—Stirring rod, test tubes or beakers.

Materials.—Nitric, sulphuric, and tartaric acids; litmus paper, iron filings.

a. Make a very dilute solution of sulphuric acid by add-ng *three drops* of the concentrated acid to 10 c.c. water in clean vessel. By means of a *clean* stirring rod bring a lrop of this solution to the tongue. What is its taste?

Note. — Whenever you taste a substance in this way always e sure that it is *greatly diluted.* Keep it in the mouth long nough to determine the taste *definitely ;* then reject it.

b. By means of the stirring rod — it must be washed fter every test — bring a drop of the dilute acid of *a* upon d and blue litmus papers. Results? A solution which rns neutral or blue litmus *red* is said to have an *acid re-ction.*

Note. — Litmus paper should not be wasted. One piece ill do for many tests, if you use only a *drop* of the liquid each me. A new place on the litmus paper must, of course, be ed at every trial. *To avoid mistakes* by reason of substances hich may have spilled upon the table, lay the litmus paper on the bottom of a *clean, inverted* beaker.

c. Try the same experiments as in *a* and *b* with nitric id. Results? With tartaric acid. In the case of the rtaric acid use the solution obtained by heating a small ystal with 5 c.c. water. Results?

d. From Experiment XVII, *i*, tell what happens when on is treated with hydrochloric acid. Gaseous product? Vrite the equation here.

From Experiment V tell what products are formed from nc and dilute sulphuric acid. Write the equation.

From Experiment VI tell what products are formed from agnesium and dilute sulphuric acid. If magnesium sulhate is $MgSO_4$, write the equation.

e. What seems to be the common gaseous product formed when metals act upon acids?

EXPERIMENT XIX.

PROPERTIES OF BASES.

Apparatus. — Same as in Experiment XVIII.

Materials. — Solid sodium hydroxide, potassium hydroxide, and calcium hydroxide, ammonium hydroxide solution, litmus, filter paper.

a. Dissolve a small piece of sodium hydroxide, NaOH, in 10 c.c. water. Rub a drop of the solution between the fingers. Result? Dilute 3 drops of this with 5 c.c. water and taste the solution, using a stirring rod. Result? Find its effect upon blue and red litmus as in Experiment XVIII, *b.* Result?

A solution which turns sensitive neutral or red litmus blue is said to have an *alkaline reaction.*

b. Repeat *a*, using potassium hydroxide instead of sodium hydroxide. Results?

c. Add 2 drops of ammonium hydroxide solution, NH_4OH, to 5 c.c. water. Note taste of dilute solution and its action on blue and red litmus.

d. Treat about 1 gram calcium hydroxide, $Ca(OH)_2$, or calcium oxide, CaO, with 10 c.c. water, stir one minute, and then filter. Examine the solution — it is called *lime-water* — as to taste, feel, and action upon blue and red litmus.

EXPERIMENT XX.

PROPERTIES OF SALTS.

pparatus. — Same as in Experiment XVIII.
aterials. — Sodium chloride, ammonium nitrate, potassium
hate, sodium acetate, sodium carbonate, disodium hydro-
phosphate.

. Treat about one cubic centimeter of sodium chloride,
l, in a test tube with 5 c.c. water. Test the solution
n blue and red litmus as in Experiment XVIII, *a* and
Results?

. Repeat *a* with ammonium nitrate, NH_4NO_3; with potas-
n sulphate, K_2SO_4; with sodium acetate, $NaC_2H_3O_2$.
ults?

Repeat *a*, using sodium carbonate, Na_2CO_3; disodium
rogen phosphate, Na_2HPO_4.

. Arrange in a table the reactions of the substances you
e examined with litmus in Experiments XVII, XVIII,
X, and XX, thus: —

FORMULA OF SUBSTANCE.	ACTION UPON RED LITMUS.	ACTION UPON BLUE LITMUS.
HCl etc.		
$NaOH$ etc.		
$NaCl$ etc.		

What element is found in every acid? What two elements are found in every basic hydroxide? What element is not present, usually, in the *salts*, i. e., the substances studied in this experiment?

EXPERIMENT XXI.

NEUTRALIZATION.

Apparatus. — Evaporating dish, stirring rod, wire gauze, ring stand.

Materials. — Litmus solution and paper, sodium hydroxide solution, dilute hydrochloric and nitric acids.

a. To 5 c.c. ten per cent sodium hydroxide solution in an evaporating dish add 1 c.c. litmus solution; then add slowly dilute hydrochloric acid until the litmus changes color.

During the addition of acid, stir constantly with a glass stirring rod. If you get too much acid, add sodium hydroxide by means of the stirring rod until the color just becomes blue again; then add a *small* drop of *very dilute* hydrochloric acid. With care you can get the litmus to assume a color intermediate between the red and the blue, viz.: a decided *lavender*. This is the color of *neutral* litmus, and its formation shows that the basic properties of the sodium hydroxide solution have been *neutralized* by the hydrochloric acid.

b. Put a drop of the solution upon red litmus, as in Experiment XVIII, *b;* upon blue litmus. Results?

c. Evaporate the solution carefully. At the end, when the water is nearly all off and spattering begins, heat with a small flame *in constant motion.*

d. Examine the product obtained in *c*, noting its taste, solubility in water, and the reaction of the solution with litmus. Results?

The substance obtained is *sodium chloride*, or common salt. Complete the equation, $NaOH + HCl = ? + ?$

e. Repeat *a*, *b*, *c*, and *d*, using dilute nitric acid instead of hydrochloric acid. Results?

If the product has the formula $NaNO_3$, complete the equation, —

$$NaOH + HNO_3 = ? + ?$$

EXPERIMENT XXII.

NORMAL AND ACID SALTS.

Apparatus. — Two evaporating dishes, burette, test tube, rubber band, filter paper.

Materials. — Pure concentrated sulphuric acid, ten per cent potassium hydroxide solution.

a. Put a small rubber band *evenly* around a test tube to mark off 5 c.c. (see Experiment I). Do not change the position of the rubber during the experiment.

b. Dilute 15 c.c. pure concentrated sulphuric acid by pouring it into 35 c.c. water; stir the mixture with a glass rod, and cool it as in Experiment XVII, *b*.

Hold your marked test tube vertically and pour in the dilute acid up to the mark. See that the *upper* edge of the rubber is just at the *lower* level of the *meniscus*, i. e., the curved surface of the liquid. Pour the 5 c.c. of acid into an evaporating dish, rinse the test tube with 5 c.c. of water, and add the rinsings to the acid in the dish.

Note what part of your evaporating dish is occupied by the resulting 10 c.c. of liquid, for comparison in *e* of this experiment. Add to the evaporating dish 1 c.c. of litmus solution.

c. Fill a burette with ten per cent potassium hydroxide solution. The burette is best fitted with rubber and a glass tip controlled by a pinch clamp. If a glass stopcock is used see that it is well lubricated with vaseline. Support the burette in a clamp, put under it a beaker, and let the liquid run out until the part of the burette below the clamp is filled with liquid. Return the liquid which ran out to the burette. Read the level of the liquid *exactly* to tenths of a cubic centimeter, having your eye in the same horizontal plane with the bottom of the meniscus. Record this reading.

d. Open the clamp of the burette *carefully*, and let the potassium hydroxide solution fall *drop by drop* into the evaporating dish of dilute acid. Stir constantly. Get the solution exactly neutral, or at any rate have only one drop of alkali in excess.

Read the burette again. How much alkali was used?

e. Evaporate the solution to about 12 c.c., and let it cool thoroughly. Result?

f. Repeat *b*, *c*, and *d* with twice the quantity of dilute acid, *i. e.*, 10 c.c., and exactly as much potassium hydroxide as was used in *d.*

What does the litmus *now* indicate? Evaporate the resulting solution to 5 c.c., and let it cool. Result?

g. Dry the solid substance obtained in *e* between filter papers. What is the general shape of the crystals? Heat one in a dry test tube. Has it crystal-water? Treat some of the crystals with 1 to 2 c.c. water in a test tube. Are they *easily* soluble? What is the reaction of the solution to litmus? Its taste?

h. Treat the crystals obtained in *f* as directed in *g*. Results? Are the crystals in the two cases alike?

How many salts does sulphuric acid form with potassium hydroxide, according to this experiment?

EXPERIMENT XXIII.

NORMAL AND ACID SALTS CONTINUED.

Apparatus. — Same as in Experiment XXII.

Materials. — Concentrated pure hydrochloric acid, ten per cent potassium hydroxide solution.

a. In the marked test tube (see Experiment XXII, *a*) measure out 5 c.c. concentrated hydrochloric acid, put this acid into an evaporating dish, and rinse the tube with 5 c.c. of water, as in Experiment XXII, *b*. Add litmus solution, and neutralize with ten per cent potassium hydroxide from the burette. Note the amount of alkali used.

b. Evaporate the neutral solution to dryness. Finally heat the evaporating dish until no fumes of any kind come off, and even the *crackling* sound — *decrepitation* — practically ceases.

Let the dish cool thoroughly.

c. Examine the product, noting its solubility in water, the taste of the solution, and its reaction with litmus.

d. Repeat *a*, *b*, and *c* with the same amount of alkali, but with twice the quantity, *i. e.*, 10 c.c., of hydrochloric acid.

Be sure to evaporate as directed in *b*.

e. Compare results with those obtained in *c*. How many salts do you get hydrochloric acid to form with potassium hydroxide?

EXPERIMENT XXIV.

NITROGEN.

Apparatus. — 100 c.c. flask, wire gauze, ring stand, clamp, stopper, delivery tube, pneumatic trough, collecting bottle.

Materials. — Sodium nitrite, $NaNO_2$; ammonium chloride, NH_4Cl.

a. Support a flask by means of a clamp about its neck, and place under it the wire gauze. Put into the flask [illegible] grams sodium nitrite, 3 grams ammonium chloride, and 20 c.c. water.

Attach the stopper and delivery tube; the delivery tube extends to a pneumatic trough containing water and an inverted collecting bottle full of water.

b. Have ready your evaporating dish full of *cold* water. Heat the flask *gently* until a regular but not too rapid stream of gas escapes. If at any time during the heating the evolution of gas (nitrogen) becomes *violent*, remove the delivery tube from the water, take away the flame and wire gauze, and bring the evaporating dish of cold water up over the bottom of the flask. Let two test tubes of gas escape (why?); then fill the bottle with it.

c. Determine the odor and color of the gas, also its relation to combustion.

The equation representing its preparation is, in part, —

$$NH_4Cl + NaNO_2 = NaCl + N_2 + H_2O.$$

EXPERIMENT XXV.

AMMONIA.

Apparatus.— Mortar and pestle, stirring rod, test tubes, 100 c.c. flask, stopper, two right-angle tubes, collecting bottles, gauze.

Materials. — Glue, slaked lime, litmus, hydrochloric acid, ammonium chloride, ammonium nitrate, ammonium sulphate, sodium hydroxide solution, potassium hydroxide solution.

a. Mix in a mortar about one-half gram glue and 2 grams slaked lime, and heat the mixture in a test tube. Hold in the mouth of the tube, without touching the tube, a piece of moist blue litmus paper. Red litmus paper. A glass rod which has been dipped into concentrated hydrochloric acid. Results? Note odor. What is it?

b. To about one-half gram ammonium chloride in a test tube add 2 c.c. ten per cent sodium hydroxide solution, and warm gently. Odor? Effect of gas on litmus? On a rod wet with concentrated hydrochloric acid?

c. Repeat *b*, using ammonium nitrate and sodium hydroxide solution. Results? Use ammonium sulphate and ten per cent potassium hydroxide solution. Results? The gas formed in the above cases is ammonia, NH_3.

d. In a 100 c.c. flask mix 10 grams powdered ammonium chloride and 20 grams powdered quicklime. Odor? Support the flask on wire gauze and attach the stopper and a delivery tube bent twice at right angles (see Experiment XVI, *a*). Have the second right-angled tube turned *upward*. On a small ring fastened high up on the ring stand, lay a piece of cardboard with a small hole in it; through the hole pass the delivery tube, and invert over the delivery tube the *dry* receiver (bottle) intended to collect the ammonia.

e. Heat *very gently*. When the bottle is full of gas, — test this by waving air from the bottle toward the nose, — cover it and place it mouth down upon the table. Fill three bottles with the gas. Now turn the end of the delivery tube down, so that it just touches the surface of 10 c.c. water in a test tube.

After a minute raise the test tube *carefully* about 2 cm. Do the bubbles of ammonia rise to the surface of the water? Why? Lower the test tube again until the delivery tube just touches the water, and continue heating the flask gently three minutes. Remove the test tube; and *then* extinguish the flame. While the flask is cooling, place between it and the wire gauze a dry cloth. Why?

f. Did you notice any change in the temperature of the water of the test tube? Explain. Save this liquid.

g. From the method of collecting the gas compare its specific gravity with that of air. Is there any evidence of water in the generating flask?

h. Test the gas in the first receiver with litmus paper — keep mouth of receiver down. Test relation of this gas to combustion. Results?

Thrust up into the receiver a glass rod which has been dipped in concentrated nitric acid. Results? The smoke is ammonium nitrate, NH_4NO_3. Write the equation.

i. Place the second bottle mouth downward in a pan of vater. Result? Explain.

j. *Warm* the bottom and sides of a clean, dry bottle having a mouth of the same size as that of the third bottle f ammonia) by moving it *quickly* to and fro in the Bunsen lame; put into it five drops concentrated hydrochloric acid, nd place over the bottle of hydrochloric acid gas thus btained, the bottle of ammonia. Hold the mouths of the ottles firmly together and reverse their positions, so that he ammonia bottle is below the other. Results? What is he product?

k. Examine the solution of ammonia made in *e.* What ffect has it upon litmus? Hold a piece of moist red litmus bout 2 cm. above the solution. Result? Explain.

Put 5 c.c. of the solution into a beaker, note the odor, and et beaker stand for twenty-four hours. Is the odor as trong as before? Inference?

l. Put about 5 c.c. of the ammonia solution of *e* into an vaporating dish, and boil it gently for five minutes. Com-are odor after boiling with that of some of the original olution.

m. Heat a small amount of ammonium chloride for some ime on a piece of porcelain or on platinum. Result?

n. The equation for the reaction which took place in *d* nd *e* is,—

$$\mathrm{Ca}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix} + \begin{matrix}\mathrm{NH_4Cl}\\\mathrm{NH_4Cl}\end{matrix} = \mathrm{Ca}\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix} + \begin{matrix}\mathrm{NH_4OH}\\\mathrm{NH_4OH}\end{matrix}\left(= \begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix} + \begin{matrix}\mathrm{H_2O}\\\mathrm{H_2O}\end{matrix}\right), \text{ or}$$

$$\mathrm{Ca(OH)_2 + 2\ NH_4Cl = CaCl_2 + 2\ NH_3 + 2\ H_2O.}$$

Where would you look for the calcium chloride?

EXPERIMENT XXVI.

NITRIC ACID.

Apparatus. — 100 c.c. flask, cork, stopper, delivery tube (in one piece), test tube, beaker, wire gauze, ring stand.

Materials. — Potassium nitrate, concentrated sulphuric and nitric acids, white silk thread, indigo solution, ferrous ammonium sulphate or ferrous sulphate, and copper nitrate.

a. Into a 100 c.c. flask place about 5 grams potassium nitrate and 10 c.c. concentrated sulphuric acid. Attach the stopper and the delivery tube. The delivery tube must be *in one piece without rubber connections.*

Put the end of the delivery tube into a test tube resting in a beaker of cold water. The test tube will serve as a *condenser.*

b. Warm the flask *gradually* over the wire gauze. Result? Color of fumes? Keep the end of the delivery tube out of the liquid which condenses in the test tube.

When no more liquid distills over, remove the delivery tube. Only then remove the flame.

The liquid collected is *nitric acid.* Complete the equation,

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + ?$$

What is the color of the acid?

c. Let the flask cool thoroughly. Result? Name the crystalline product. Finally, add water and pour the resulting solution into the sink.

d. Add 1 c.c. of the nitric acid you have made to 1 c.c. of water, and test the action of a drop (use the glass rod) upon litmus. Result?

Into your diluted acid put a piece of white woolen yarn, and warm gently. Remove the yarn. How has it *changed?*

To 1 c.c. of your dilute acid add a few drops of indigo solution. Result?

e. What color does your undiluted acid give to the skin? Will ammonium hydroxide remove the stain?

f. Treat about 2 c.c. of ferrous ammonium sulphate or of ferrous sulphate in a test tube with 15 c.c. water and shake vigorously. Take 5 c.c. *of this solution* in a test tube, add two drops of dilute nitric acid, incline the tube at an angle of about forty-five degrees, and pour about 3 c.c. concentrated sulphuric acid down the side of the tube. Describe what takes place where the concentrated acid, which is below, meets the solution.

g. Repeat *f*, using a solution of *potassium nitrate* instead of nitric acid. Result? Repeat again with *cupric nitrate* instead of the acid. Result?

h. If the test just tried is a general one for *all nitrates*, how would you proceed to test a solution for the presence of a nitrate or nitric acid?

EXPERIMENT XXVII.

NITRITES.

Apparatus. — Iron dish, stout iron wire, beaker, test tubes.

Materials. — Potassium nitrate, lead, filter paper, dilute sulphuric acid.

a. Melt together in a shallow iron dish 10 grams potassium nitrate, KNO_3, with about 20 grams of lead. Keep the mixture at red heat, and stir twenty minutes with a stout iron wire or a nail held in iron tongs.

b. When the mass is cool add 20 c.c. water, heat to boiling for a few minutes, take out the unused lead, and then filter.

The residue on the filter is lead oxide, PbO. Its color? The filtrate contains potassium *nitrite*, KNO_2, and unchanged nitrate. The reaction is a *reduction* of potassium nitrate by lead, as is shown in the equation,

$$KNO_3 + Pb = KNO_2 + PbO.$$

c. Treat the solution of potassium nitrite from *b* with dilute sulphuric acid. Result? Treat some potassium nitrate solution in a test tube with dilute sulphuric acid, and compare results.

d. The brown gas is nitrogen trioxide, N_2O_3, formed as shown by the equation,

$$KNO_2 + H_2SO_4 \longrightarrow KHSO_4 + HNO_2.$$
$$2\ HNO_2 = N_2O_3 + H_2O.$$

EXPERIMENT XXVIII.

NITROGEN TETROXIDE.

Apparatus. — Test tubes, doubly bent delivery tube.

Material. — Powdered lead nitrate, $Pb(NO_3)_2$.

a. Heat 5 grams powdered lead nitrate carefully in a test tube (use a holder), keeping the tube *in constant motion.* Result?

When the tube is full of gas, attach a stopper and a delivery tube with its longer arm *turned down.* Fill a dry test tube with the evolved gas by displacement of air.

b. Invert the test tube of gas in a beaker of water, and leave it a few minutes. Result? Test the residual gas with a pine splinter having a spark on the end of it. Result?

c. The brown gas is *nitrogen dioxide*, NO_2, mixed with *nitrogen tetroxide*, N_2O_4.

The equation is,

$$Pb(NO_3)_2 = PbO + N_2O_4 \ (= 2\ NO_2) + O.$$

d. The lead oxide in the test tube may nearly all be removed by adding to the cold tube dilute nitric acid and heating *carefully.*

EXPERIMENT XXIX.

NITRIC OXIDE.

Apparatus. — Generating flask (250 c.c.), two stoppers (one two-holed and one one-holed), funnel tube, delivery tubes, pneumatic trough, wide-mouth collecting bottles, cardboard or glass covers.

Materials. — Copper (granulated or turnings), nitric acid, ferrous sulphate, splinter of pine, red phosphorus.

a. Into a generating flask or bottle put enough granulated copper to cover the bottom. Attach stopper containing funnel tube and delivery tube. Add through the funnel tube enough dilute nitric acid to immerse the lower end of the tube, and then concentrated acid, as necessary, to give brisk action. The gas produced is *nitric oxide*, NO. *If the acid is too concentrated, considerable nitrogen tetroxide is produced.*

b. Fill a bottle over water with the gas, and expose it to the air. Result? From the result tell why the gas in the generating flask was originally brown.

c. Pass the gas about three minutes into 10 c.c. concentrated ferrous sulphate solution in a test tube. Result? Save the solution for *g*.

d. Collect a second and a third bottle full of the gas over water. Cover one of the bottles, remove it from the water, turn it mouth upward, and put into it a lighted splinter. Result?

e. Repeat *d* with the last bottle of the gas, using a deflagrating spoon containing *briskly burning* red *phosphorus*, instead of the splinter. Compare results. Is nitric oxide a supporter of combustion, or not?

f. Attach to the test tube of solution from *c* a one-holed stopper and a delivery tube. Warm gently and collect the evolved gas over water in a test tube. Expose the gas to the air. Result? Conclusion?

The brown liquid obtained in *c* contains a compound of ferrous sulphate and nitric oxide.

See Experiment XXVI, *f*, where the formation of a brown ring of this compound was used as a test for nitric acid and the nitrates.

g. Pour 25 c.c. of the solution (its color?) left in the generating flask into a beaker, add any unused copper, and let the beaker stand (in a gas chamber if possible) until all action ceases. There should be an *excess* of copper. Pour the liquid into an evaporating dish, and evaporate on a wire gauze to about 10 c.c. Dip into the liquid a glass rod, and see if the liquid which sticks to the rod will solidify on cooling. If so, let the dish cool; if not, evaporate off about 2 c.c. more, and try again. Result?

The substance obtained is *cupric nitrate*, $Cu(NO_3)_2$.

The equation is,

$$3\ Cu + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO.$$

EXPERIMENT XXX.

NITROUS OXIDE.

Apparatus.—Test tubes, stopper, delivery tube, pneumatic trough, clamp, ring stand, collecting bottle.

Materials.—Ammonium nitrate, pine splinter.

a. Into a test tube provided with stopper and delivery tube put about 10 grams ammonium nitrate, and fasten the test tube by a clamp to the ring stand. The test tube should be inclined at an angle of about forty-five degrees.

Invert a bottle of water (best *warm*) in the pneumatic trough, but do not put the delivery tube into the water until *c*.

b. Heat the test tube *gently* with a moving flame. Result? Warm more. Result?

When a steady stream of gas is evolved, hold over the end of the delivery tube a cold and dry beaker. What collects in it?

c. Now put the end of the delivery tube into the pneumatic trough, and fill the collecting bottle with the gas. The gas is *nitrous oxide*, N_2O.

Set the bottle of gas mouth upward and covered upon the table, and then fill a test tube with the gas.

Note. — *Be sure to take the delivery tube out of the water before you remove the flame.*

d. To the test tube of gas add 5 c.c. *cold* water, close the tube tightly with the thumb, and shake vigorously. Open the tube under water. Result?

e. What is the odor of the gas in the bottle? Insert into it a pine splinter with a glowing tip. Result?

What gas resembles nitrous oxide in its *vigorous* support of combustion?

EXPERIMENT XXXI.

PHYSICAL PROPERTIES OF SULPHUR.

Apparatus. — Test tubes, filter, funnel, evaporating dish, beaker.

Materials. — Powdered sulphur, carbon disulphide.

a. Test the solubility of sulphur as follows: In a test tube shake 1 c.c. powdered sulphur with 5 c.c. water; filter, and evaporate the filtrate in an evaporating dish. Result? Conclusion?

What is the odor of sulphur? Its taste?

b. Treat *not more than 1 c.c.* powdered sulphur in a test tube with 5 c.c. carbon disulphide.

Caution. — Carbon disulphide is *inflammable. Do not bring it near a flame.*

Close the test tube with the thumb, and shake it thoroughly. Result? Pour the contents of the tube into a *small* beaker, and set this aside in a gas chamber (*not in your cupboard*) until the next laboratory period. Result? What is the shape of the larger crystals?

c. Fill a test tube one-third full of sulphur, hold it inclined at an angle of about forty-five degrees, and heat it carefully. Note the changes through which the sulphur passes as you raise its temperature.

What is the color of the liquid formed by melting the sulphur? Is it *viscous* (thick) or *limpid* (thin; easily poured)? Pour a drop of it into water. Color of the product? Is it hard or soft? Sulphur melts at about 114° C.

d. What change does the sulphur undergo when you heat it further? Tilt the test tube to an *almost* horizontal position from time to time *until you find the point at which the liquid cannot be poured.* Then continue heating, and notice that the sulphur becomes limpid again.

Finally, heat the sulphur to boiling. You will know that boiling is taking place when you see the dark brown liquid condensing upon the upper (cooler) parts of the tube. Sulphur boils at 446° to 448° C.

e. Pour the boiling sulphur into a beaker of *cold* water. Result? Color of the product? Is it hard or soft? Elastic or brittle? Keep this for several weeks, noting from day to day any changes that take place.

EXPERIMENT XXXII.

CHEMICAL PROPERTIES OF SULPHUR.

Apparatus.—Deflagrating spoon, 250 c.c. bottle, cardboard, test tube.

Materials.—Sulphur, blue litmus paper, powdered iron.

a. Put about 1 c.c. powdered sulphur in a deflagrating spoon, heat it in the flame until it burns briskly, and then put the spoon into a bottle of air. Keep the bottle covered with cardboard having a hole in it for the handle of the spoon.

Let the sulphur burn as long as it will. Name the product of the combustion. What is its physical state? Its odor? Try its effect upon *wet* blue and red litmus papers.

b. Mix in a mortar 5.6 grams powdered iron and 3.2 grams powdered sulphur, and put the mixture into a test tube. Heat the lower portion of the tube for a moment in the Bunsen flame. Result? When action begins, withdraw the test tube from the flame. Describe all that takes place.

c. When the product is cool, break the test tube, and remove the solid lump. Describe the product. It is *ferrous sulphide*, FeS.

Write the equation for its formation. Save the solid for Experiment XXXIII.

EXPERIMENT XXXIII.

HYDROGEN SULPHIDE.

Apparatus. — Test tubes, stopper, and delivery tube.

Materials. — Ferrous sulphide from Experiment XXXII; dilute sulphuric acid; solutions of cupric sulphate, barium chloride, lead nitrate, sodium hydroxide, and litmus.

Note. — Perform this experiment in a gas chamber, or where there is a *good* draught.

a. Treat the lump of ferrous sulphide made in Experiment XXXII with dilute sulphuric acid in a test tube. Result? *The gas is hydrogen sulphide,* H_2S. Attach a stopper and delivery tube, and fill a test tube held mouth upward with the gas. Apply a match to the test tube. Result? Note odor of the burning gas. Result? Complete the equation,

$$2\ H_2S + 3\ O_2 = 2\ H_2O + ?$$

b. Pass the hydrogen sulphide gas from the generating tube into 5 c.c. dilute cupric sulphate ($CuSO_4$) solution in a test tube. Result? Continue about one minute.

Now see that the delivery tube is clean, and pass the gas three or four minutes into 15 c.c. water in a test tube. Then wash out the generating tube *thoroughly.*

c. Filter the test tube of cupric sulphate into which you have passed hydrogen sulphide. Compare the color of the filtrate with that of the cupric sulphate taken. Conclusion?

The black residue is cupric sulphide, CuS. Write the equation for the action of *hydrogen sulphide* upon *cupric sulphate.*

d. Add a few drops of the hydrogen sulphide solution to 2 c.c. lead nitrate solution, $Pb(NO_3)_2$. Result? If the insoluble product is lead sulphide, PbS, write the equation.

Repeat, using *cadmium sulphate* solution in place of *lead nitrate.* Result? If the insoluble product is *cadmium sulphide,* CdS, write the equation.

e. Test the reaction of the hydrogen sulphide solution with red and blue litmus papers. Results? Conclusion?

Add to the remainder of the hydrogen sulphide solution 1 c.c. sodium hydroxide solution. The solution now contains *sodium sulphide*, Na_2S. Write the equation.

f. How would you make ammonium sulphide solution, $(NH_4)_2S$? Write the equation.

EXPERIMENT XXXIV.

SULPHUR DIOXIDE.

Apparatus. — 100 c.c. flask, ring stand, wire gauze, stopper and delivery tube, 2 collecting bottles, test tubes, beaker, evaporating dish.

Materials. — Granulated copper, concentrated sulphuric acid, red flower, red cheese cloth, crystals of cupric sulphate, dilute sulphuric acid, sodium hydroxide solution, litmus paper, concentrated nitric acid, potassium permanganate and potassium dichromate solutions.

a. In a 100 c.c. flask put about 5 grams copper and add 25 c.c. concentrated sulphuric acid. Support the flask in a ring stand, upon wire gauze, and attach a stopper and a doubly bent delivery tube reaching *almost* to the table.

b. Heat the flask *carefully.* When brisk effervescence begins, moderate the heat. Collect 2 bottles of the gas as you did chlorine in Experiment XVI, *b.* Tell when each bottle is full by the odor. Stopper the bottles. Collect, also, a test tube of the gas and put it, mouth down, into a beaker of water. Explain the result.

Wave a little of the escaping gas toward the nose. Odor?

The gas is ***sulphur dioxide***, SO_2.

c. Put the end of the delivery tube ***just at the surface*** of 10 c.c. water in a test tube. When the gas is coming off freely, raise the test tube about 1 cm. What evidence is there that the gas is dissolving? Lower the test tube to its former position and keep it there 5 minutes. Then remove the delivery tube from the water, extinguish the flame, and let the generating flask cool in position, *out of contact with the wire gauze.*

Stopper the test tube containing the solution of the gas, and keep it.

d. Into one bottle of sulphur dioxide gas put a few petals of some red flower, *e. g.*, a carnation; also a small piece of wet, red cloth such as you used with chlorine in Experiment XVI, *d.* Results?

Test the action of sulphur dioxide upon blue litmus paper. Result?

e. To the second bottle of sulphur dioxide add 4 drops of concentrated nitric acid, stopper the bottle, and shake it. Results? Add 5 c.c water, stopper once more, shake, and pour the liquid into a test tube. Save this for Experiment XXXVI, *c.*

f. Note the taste of a drop of the sulphur dioxide solution made in *c.* What is the action of 1 c.c. of it upon 1 c.c. potassium permanganate solution ($KMnO_4$)? Repeat with potassium dichromate solution instead of potassium permanganate. Result?

***Sulphur dioxide** solution contains sulphurous acid*, H_2SO_3.

g. ***Neutralize*** the remainder of the sulphurous acid in an evaporating dish with 10% sodium hydroxide solution and evaporate to dryness. The resulting substance is *sodium sulphite*, Na_2SO_3. Describe it.

Complete the equation,

$$2\ NaOH + H_2SO_3 = ? + ?$$

h. Treat the sodium sulphite in a test tube with a little dilute sulphuric acid, and warm. Note the odor.

The sulphite is decomposed by the acid thus:—

$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2SO_3$ (*i. e.*, $SO_2 + H_2O$).

i. When the generating flask is *cold*, add to it 25 c.c. water, shake *carefully*, and heat the flask *cautiously* over wire gauze. Filter the resulting liquid. What is the color of the filtrate? Concentrate it to about 15 c.c., and let it cool. Result? Compare the product with blue vitriol, $CuSO_4 . 5\ H_2O$. Complete the equation,

$$Cu + 2\ H_2SO_4 = 2\ H_2O + ? + ?$$

EXPERIMENT XXXV.

SULPHURIC ACID.

Apparatus.—File or blue paraffin pencil, test tube, beaker, balances.

Materials.—Concentrated sulphuric acid.

a. By means of a file or a blue paraffin pencil mark off about 10 c.c. on a clean, dry test tube, set the tube in a clean beaker, and get the weight of both test tube and beaker together. Now fill the tube up to the mark with concentrated sulphuric acid, wipe off any acid adhering to the mouth of the test tube, and get the weight of acid + beaker + test tube.

Return the acid to the bottle, rinse the test tube, and dry it on the outside. Then fill the tube up to the mark with water, and get the weight of water + beaker + test tube.

Record your results thus: —

Grams

Weight of test tube + beaker + sulphuric acid =
Weight of test tube + beaker =
∴ weight of sulphuric acid taken =
Weight of test tube + beaker + water =
Weight of test tube + beaker =
∴ Weight of water taken =

From the results calculate the specific gravity of your sulphuric acid.

b. Heat *one* drop — no more — of concentrated sulphuric acid in an evaporating dish over wire gauze. Result?

c. Put into a test tube a splinter of wood and add 5 c.c. concentrated sulphuric acid. Let stand 15 minutes. Try the effect of a drop of concentrated sulphuric acid on paper; upon cotton cloth. Wait for the result if it is not immediate. Results?

d. Into a small beaker put 10 grams sugar and 5 c.c. water, and stir thoroughly. Now add 10 c.c. concentrated sulphuric acid. Results? Describe the product.

EXPERIMENT XXXVI.

SULPHATES.

Apparatus. — Test tubes.

Materials. — Concentrated sulphuric acid; solutions of barium chloride, cupric sulphate, sodium sulphate; dilute hyhrochloric acid; liquid from Experiment XXXIV, *e*.

a. To 10 c.c. water in a test tube add 1 c.c. concentrated sulphuric acid. Result? Heat the diluted acid to boiling, and add 5 c.c. barium chloride solution, $BaCl_2$. Result?

The precipitated substance is barium sulphate, $BaSO_4$. If the other product is hydrochloric acid, write the equation.

Let the precipitate settle, pour off the *supernatant* liquid, and add 10 c.c. dilute hydrochloric acid to the precipitate. Does the precipitate dissolve?

b. Repeat *a*, using instead of dilute sulphuric acid 5 c.c. of a solution of cupric sulphate, $CuSO_4$. Results? Equation?

Repeat again, using 5 c.c. of sodium sulphate solution, Na_2SO_4, with 5 c.c. barium chloride solution. Result? Equation?

Note. — *In general*, if a solution gives with barium chloride solution a white precipitate *insoluble in hydrochloric acid*, we are *reasonably* sure that the unknown solution contains sulphuric acid or a *sulphate.*

c. Treat the liquid obtained in Experiment XXXIV, *e*, with barium chloride solution. Result? What effect did nitric acid have upon the sulphur dioxide? Complete the equation,

$$SO_2 + O + H_2O \longrightarrow$$

EXPERIMENT XXXVII.

CARBON.

Apparatus. — Tongs, test tubes, iron dish with a cover, beaker.

Materials. — Charcoal (lumps and powder), graphite (pencil lead), soft coal, hydrogen sulphide solution, litmus solution, brown sugar, animal charcoal.

a. Hold a piece of charcoal in the Bunsen flame (use tongs) and describe its combustion. Repeat with *graphite* (pencil lead) and with soft coal.

b. Fill an *old* test tube one-fourth full of bits of wood, and heat. Results? Bring a burning match to the mouth of the tube. Result? Describe the other products. What is the residue?

c. Hold a piece of wood-charcoal under water in a beaker for 2 minutes. What appears on its surface? Conclusion?

d. Heat powdered wood charcoal or animal charcoal for 5 minutes in a covered iron dish. Let it cool, and add 2 c.c. of it to 5 c.c. *hydrogen sulphide* solution. Shake thoroughly and filter. Compare odor of filtrate with that of the solution taken. Conclusion?

e. Boil 5 c.c. *litmus* solution 2 minutes with 2 c.c. of the freshly ignited charcoal, and filter. Result? *Repeat*, using 5 c.c. of a solution of brown sugar with 2 c.c. fresh charcoal. Result?

EXPERIMENT XXXVIII.

CARBON DIOXIDE, I.

Apparatus. — Generating flask, stopper with thistle tube and delivery tube, pneumatic trough, beaker, test tubes, and collecting bottles.

Materials. — Marble, hydrochloric acid, litmus, lime-water.

a. Place in a flask enough marble (a form of *calcium carbonate*, $CaCO_3$) to cover the bottom, add enough water to close lower end of the thistle tube, insert stopper, and add concentrated hydrochloric acid through the thistle tube. Add more acid when it is needed. Collect the *carbon dioxide* (CO_2) over water, rejecting the first bottle of the gas. See, also, Experiment XV.

b. Put into a bottle of the gas wet litmus paper (red and blue) and a burning match. Results?

c. Pour a bottle of the gas into a beaker of air. Test the gas in the beaker with a burning match. Result? Conclusion as to the specific gravity of the gas?

d. Fill a test tube with the gas by air displacement, add 5 c.c. *cold* water, close tube securely with thumb, shake vigorously, and open under water. Result? Conclusion?

e. Pass the gas into lime-water, $Ca(OH)_2$. Result? Let the precipitate settle. It is *calcium carbonate.* Its formation with lime-water is a **test** for carbon dioxide (*cf.* Experiment VII, *e*). Now pass a vigorous stream of the gas into the tube five minutes. Result? Boil the contents of the tube. Result?

EXPERIMENT XXXIX.

CARBON DIOXIDE, II.

Apparatus. — Beakers, delivery tube, test tubes.

Materials. — Lime-water, sodium bicarbonate, tartaric acid.

a. Mix 2 c.c. each of *sodium bicarbonate* ($NaHCO_3$) and *tartaric acid* ($H_2C_4H_4O_6$) in a mortar. Is a change apparent? Put half of the powder into a test tube, and add water. Result? Identify the gas.

b. Put the remainder of the mixture from *a* in a test tube, add 10 c.c. water, and, as soon as you are able, imprison the gas by holding your thumb upon the mouth of the test tube. Effect upon the effervescence? Now remove your thumb. Effect? Explain.

c. Blow your breath through a delivery tube into 5 c.c. lime-water. Result? Conclusion?

d. Expose 5 c.c. *clear* lime-water to the air for several hours. Result? How does carbon dioxide get into the air (*cf.* Experiment VII, *e*)?

EXPERIMENT XI.

REDUCTION BY CARBON. EFFECT OF HEAT ON CARBONATES.

Apparatus. — Ignition tube, delivery tube, rubber connector, test tubes.

Materials. — Lead monoxide, powdered charcoal, lime-water, magnesite.

a. Mix 1 c.c. lead monoxide, PbO, with one-third its volume of powdered charcoal, on *smooth* paper. Into the ignition tube put enough of the mixture to make a layer 1 cm. thick, support the tube almost horizontally, and attach a delivery tube leading into 5 c.c. lime-water. Heat the lead monoxide *persistently* for 10 minutes, cool it, and pour it out on the table. Result? What gas was evolved? Write the equation.

b. Fill the ignition tube one-fifth full of chips of *magnesite*, $MgCO_3$, and set it up as in *a.* Heat persistently. What gas is evolved? What, then, does the residue contain? Write the equation.

EXPERIMENT XLI.

FLAMES.

Apparatus. — Bunsen burner and tongs.

Materials. — Candle, piece of porcelain, white paper.

a. Examine carefully the non-luminous flame. Sketch a vertical section of it *as you see it.* Make drawing 4 cm. long.

b. Do the same with a *luminous* Bunsen flame 2 cm. high. Repeat with a candle flame.

c. Press the colorless Bunsen flame for a moment upon paper lying on your table. The paper should not burn up. Result?

Hold a piece of glass tubing about 1 dm. long at an angle of 45°, with the lower end inside the central part of the non-luminous flame, and apply a lighted match to the other end. Result? What do these experiments show as to the inner region of the flame?

d. Hold a piece of porcelain (broken evaporating dish) by means of tongs in the luminous flame. Result? What substance is in excess here? Now hold the porcelain in the colorless flame for some time. Result? What is in excess in this flame?

EXPERIMENT XLII.

WEIGHT OF A LITER OF OXYGEN.

paratus. — A strong test tube, two one-liter bottles, bent tubes, pinch-clamp, graduated cylinder, balances.

terials. — Powdered, chemically pure potassium chlorate nanganese dioxide, dried at 120° C. Water at room erature.

Set up the apparatus shown in Fig. 64. *A* is a test having a strong flare, so that it can be slipped tightly a rubber stopper. a liter bottle fitted a two-hole rubber er. The longer reaches *almost* to ottom of *B*, and nnected at *F* with ber tube reaching e bottom of the C. The rubber may be closed by pinch-clamp *F*. st fill the bottle th water having the temperature of the room, and then e long tube and the rubber tube by sucking at *D*, *A* removed. Then close the pinch-clamp.

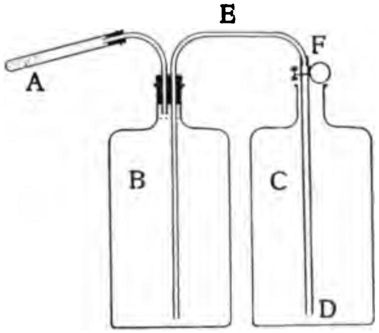


Fig. 66.

Into the test tube *A* put about 5 c.c of a mixture of parts of powdered, chemically pure potassium chlor- nd manganese dioxide; they must have been dried at

120° C. for at least an hour. Get the weight of test tube and mixture *accurately* on the balances, and record it.

c. See that the stopper is pressed securely into the mouth of *B*, and then slip *A* carefully, but tightly, over its stopper. Now put about 50 c.c. water into *C*, raise *C* so that the water in *B* and *C* are at the same level, open the pinch-clamp one minute, and then close it. Then put *C* down on the table. Take the rubber tube carefully out of *C* and get the volume of the water in *C*; then pour the water back into *C*, and put the rubber tube in place. Now open the pinch-clamp, and hang it upon the glass tube at *E*. Do not allow the lower end of the rubber tube to get above the surface of the water in *C*. Why?

d. Heat the mixture in *A* *gently*, beginning at the upper part of the mixture. The evolved gas forces water from *B* into *C*. When *C* is about half full, stop heating, and let *A* cool to room temperature. Then raise *B* or *C*, as necessary, to make the water levels in both the same (be sure to keep the lower end of the rubber tube under water), close the rubber tube with the pinch-clamp, and get the volume of the water in *C*. This, *minus* the original volume, equals the volume of gas collected in *B*.

Find the barometric height, subtract from it the correction for the pressure of water vapor (see Appendix), and find, also, the temperature of the gas. Finally, weigh *A* and its contents *accurately*.

e. Record your results thus: — *Grams.*

Weight of test tube + contents at first =
Weight of test tube + contents afterward = ——
∴ Weight of oxygen =
Volume of oxygen at ° C. and mm. = c.c.
∴ Volume of oxygen at 0° C. and 760 mm. = c.c.
Weight of oxygen obtained : weight of a liter at 0° C. and 760 mm. :: volume (at 0° C. and 760 mm.) : 1,000 c.c.

EXPERIMENT XLIII.

BROMINE.

Apparatus. — Beaker. 100 c.c. flask. test tubes.

Materials. — Potassium bromide. powdered manganese dioxle, dilute sulphuric acid. litmus paper. calico. carbon disulide, chlorine-water. sodium hydroxide.

Caution. — If possible. work in a gas-chamber or hood.

a. Into a flask put an eighth of a test tube of potassium omide (KBr) crystals, half as much powdered manganese oxide, and half a test tube of dilute sulphuric acid. Suprt the flask over wire gauze, and attach the cork stopper d a doubly bent delivery tube reaching into a test tube ree-fourths full of cold water. The delivery tube must without rubber connections. The test tube should rest a beaker of water.

b. Warm the flask *carefully* until a dark brown distillate sses over. Is it heavier or lighter than water? **Do not hale the vapor,** and do not get liquid bromine on your nds.

When no more bromine comes over, remove **first** the devery tube and then the flame. The light-brown solution "bromine-water."

c. Wave the air from the test tube toward the nose. dor of bromine? Pour off as much bromine-water as posble without pouring out the bromine, and add more water the bromine. Pour a few drops of the bromine-water pon litmus paper and upon colored calico. Results?

d. To 3 c.c. water in a test tube add 1 c.c. *carbon disul-*

phide, close tube with thumb, and shake vigorously. Results? Where is the carbon disulphide? Now add ¼ c.c. bromine-water and shake again. Result to the color of the water? To that of the carbon disulphide? *This effect on the carbon disulphide is a test for* free *bromine.*

e. To 5 c.c. of potassium bromide solution add 1 c.c. carbon disulphide and shake. Result? Now add two or three drops of *chlorine-water* (made as in Experiment XVI, *i*), close the tube, and shake it as before. Results? Action of chlorine on potassium bromide? Equation?

f. To the liquid bromine in the test tube add sodium hydroxide solution, a c.c. at a time, shaking thoroughly. (Do not close the tube with the thumb!) Result? The equation is, —

$$2\,NaOH + 2\,Br \longrightarrow NaBr + \underset{\substack{\text{sodium}\\ \text{hypobromite}}}{NaBrO} + H_2O.$$

EXPERIMENT XLIV.

IODINE AND HYDRIODIC ACID.

Apparatus. — Test tubes, beaker, flask.

Materials. — Potassium iodide, manganese dioxide, sulphuric acid, iodine, carbon disulphide, chlorine- and bromine-water, starch, alcohol, hydrogen sulphide, silver nitrate solution, sodium carbonate, litmus.

a. Powder *potassium iodide* (KI), mix 1 c.c. of it with a c.c. of manganese dioxide, add 2 c.c. water and then 1 c.c. concentrated sulphuric acid. Result? When the action slackens, warm the tube gently, and then let it cool. Describe what you find in the tube? It is *iodine.* Compare its preparation with that of chlorine and bromine.

b. Warm a crystal of iodine (*gently,* not to boiling) with 10 c.c. water for a few seconds. Does the iodine dissolve *readily?* Cool the water and add 3 c.c. of it to 1 c.c. carbon disulphide. Shake the closed tube. Result? *This is a test for* **free** *iodine.* Save the iodine solution.

c. Shake 5 c.c. potassium iodide solution with 1 c.c. carbon disulphide. Result? Add a drop of chlorine-water and shake again. Result? What effect has chlorine upon potassium iodide? *Repeat,* using bromine-water instead of chlorine-water. Write both equations.

d. Make a **starch solution** as follows: Mix 2 c.c. powdered starch with 5 c.c. cold water, and pour the emulsion into 30 c.c. boiling water. Boil for a minute or two, and then cool. To 3 c.c. of the solution add a drop of the iodine solution of *b*, shaking. Result?

To 3 c.c. of the starch solution add one drop of a potassium iodide solution and then one drop of chlorine- or bromine-water. Result?

e. Heat a crystal or two of iodine in a dry, inclined test tube. Result? Let cool. Result? Effect of iodine on the skin? On wood and paper?

f. To the iodine of *e* add 5 c.c. *ethyl alcohol,* C_2H_5OH. In which is iodine more soluble, water or alcohol? An alcoholic solution is often called a *tincture.*

g. To one-half a c.c. of powdered iodine in a flask add 20 c.c. water and then pass in hydrogen sulphide (gas-chamber!) until the iodine disappears. Results? Boil the solution gently two minutes, and filter it. Identify the precipitate by igniting a little on a piece of porcelain. Odor? Test the filtrate with red and blue litmus. Results? Add a drop of it to 1 c.c. silver nitrate solution. Result? Add some to 1 c.c. solid sodium carbonate. Result? What substances are formed from hydrogen sulphide and iodine? Equation?

EXPERIMENT XLV.

COMPARISON OF THE HALOGEN ACIDS.

Materials. — Potassium chloride, bromide, and iodide; concentrated sulphuric acid, litmus.

a. Three test tubes have small amounts of potassium chloride, bromide, and iodide, respectively; treat each with a few drops of concentrated sulphuric acid. Results? Blow your breath across the mouth of each tube. Result? Test the gas of each with blue litmus. Result? Note carefully the odor of each gas. What odors beside that of the acid do you get in the tube of potassium iodide? Heat this tube. Result?

b. Which tube gives a colorless gas? What colors the gas in each of the two other cases? From the amount of coloration, tell which of the three halogen acids is most easily decomposed into its elements. Which least.

EXPERIMENT XLVI.

HYDROGEN PEROXIDE.

Materials. — Hydrochloric acid, barium peroxide, starch solution, potassium iodide solution, manganese dioxide, potassium permanganate, ether, potassium dichromate solution, splinter.

a. To 25 c.c. water add 5 c.c. concentrated hydrochloric acid and then 3 grams powdered *barium peroxide*, BaO_2, a little at a time, stirring. Filter the solution; it should contain *hydrogen peroxide*, H_2O_2.

b. To 5 c.c. starch solution add a drop of potassium iodide solution, and then a few drops of the hydrogen peroxide solution. Result?

c. To 3 c.c. of the solution of *a* add 3 c.c. ether. Do they mix? Is the ether above or below? Now add *one drop* of potassium dichromate solution. Close tube and shake *gently*. Result?

d. To 5 c.c. of the hydrogen peroxide solution add 1 c.c. powdered manganese dioxide. Result? Test gas with a glowing splinter. Result?

e. To three crystals of potassium permanganate in a test tube add 2 c.c. water and then 5 c.c. of the hydrogen peroxide solution. Result? Test with glowing splinter. Result?

EXPERIMENT XLVII.

PHOSPHORUS AND PHOSPHORIC ACID.

Apparatus. — Test tubes, small ignition tube, tongs, evaporating dish, file.

Materials. — Red and yellow phosphorus, carbon disulphide, filter paper, phosphoric acid, ammonium hydroxide; silver nitrate, disodium hydrogen phosphate, magnesium sulphate, ammonium chloride, and calcium chloride solutions.

Caution. — Ordinary, yellow phosphorus must be handled *only with tongs*, **never** with fingers! It must be kept and cut *under water*. No pieces of it must get into your locker; and every dish that has contained phosphorus must be *heated*, so that the phosphorus may be completely burned.

Do not bring carbon disulphide near a flame!

a. Put half a c.c. of red phosphorus into a test tube, and add 3 c.c. carbon disulphide. Result? Filter, and let the carbon disulphide evaporate, without heating, in a hood, or where its vapor will not get near a flame. Result? Was any phosphorus dissolved?

To 3 c.c. carbon disulphide add a piece of *yellow* phosphorus not larger than *a grain of wheat.* Shake carefully a few minutes. Result? Pour the solution, *every drop of it*, upon a piece of filter paper laid flat on a ring of the ring stand. Let the carbon disulphide evaporate without heating it. Result? Rinse the test tube before putting it away.

b. Into a small ignition tube put a layer of red phosphorus not more than 5 mm. thick, hold tube horizontal (tongs), and *gently* heat end containing the phosphorus. What collects on the cold part of the tube? When the tube is cold, make a file-mark just below the deposit, and break the tube. Rub the deposit with a match stick. Result? Conclusion? *Finally*, heat both tubes red hot, so as to burn up all the phosphorus. Throw the pieces into iron or crockery jars.

c. To 5 c.c. water add 1 c.c. concentrated (ortho) phosphoric acid, *neutralize* in an evaporating dish (use litmus) with ammonia, and add silver nitrate solution. Result? The precipitate is *silver orthophosphate*, Ag_3PO_4. Write the two equations.

Dissolve 2 c.c. powdered *sodium hydrogen phosphate* in 10 c.c. water. To half of the solution add calcium chloride solution. Result? The product is *secondary calcium phosphate*, $CaHPO_4$. Equation?

d. To 5 c.c. *magnesium sulphate* solution add 1 c.c. ammonia-water and 1 c.c. ammonium chloride solution, and then the disodium hydrogen phosphate solution from *c.* Result? The product is *magnesium ammonium phosphate*, $NH_4MgPO_4 . 6H_2O$.

(1) $Na_2HPO_4 + NH_4OH \longrightarrow Na_2NH_4PO_4 + H_2O.$

(2) $Na_2NH_4PO_4 + MgSO_4 \longrightarrow MgNH_4PO_4 + Na_2SO_4.$

EXPERIMENT XLVIII.

ARSENIC.

Apparatus.—Small ignition tube, tongs, test tube, beaker.

Materials.—Arsenic trioxide (powdered), charcoal, hydrochloric acid, hydrogen sulphide, ammonium sulphide, sodium hydroxide solution.

a. Into a small ignition tube put powdered *arsenic trioxide*, As_2O_3, to the depth of 5 mm. Hold the tube *horizontal* and at the *side* of the flame, so as to heat only the end containing the powder. What happens? Now slip into the tube, *almost* to the arsenic trioxide, a piece of charcoal about 2 cm. long. Heat the charcoal red hot (have tube horizontal), and then incline the tube slightly so as to heat the arsenic trioxide while keeping the charcoal red hot. Result? Effect of charcoal upon the oxide? Equation? How does the oxide come into contact with the charcoal? *Sublime* the arsenic obtained.

b. Heat half a c.c. of arsenic trioxide with 8 c.c. dilute hydrochloric acid to gentle boiling. Result? Equation? Pour off from any undissolved material, and pass in hydrogen sulphide for a minute. Result? If visible product is *arsenic trisulphide*, As_2S_3 (its color?), write equation. Let settle, pour off supernatant liquid, and add 5 c.c. *ammonium sulphide* to residue, shaking. Result? (CAUTION. — Do not get *ammonium sulphide on your hands!*) The product now formed is *ammonium sulpharsenite*, $(NH_4)_3AsS_3$; it is soluble. Treat solution with an excess of dilute hydrochloric acid in a beaker. Result?

c. Treat half a c.c. of arsenic trioxide with sodium hydroxide solution. Warm carefully. Result? The solution contains *sodium arsenite*, Na_3AsO_3. From *b* and *c* would you say arsenic trioxide has *acid*, or *basic*, properties?

EXPERIMENT XLIX.

ANTIMONY.

Apparatus. — Mortar and pestle, funnel, ignition tube.

Materials. — Antimony, concentrated nitric and hydrochloric acids, hydrogen sulphide, ammonium sulphide, antimony trioxide.

a. What is the color of metallic antimony? Is it heavy or light? Powder a small piece, and treat part of it in a test tube with concentrated nitric acid. Results?

b. Treat the remainder of the powdered antimony of *a* with 3 c.c. concentrated hydrochloric acid and 1 c.c. concentrated nitric acid. Warm to start the action, if necessary. The solution contains *antimony chloride*, $SbCl_3$. Let action continue for ten minutes; then add 15 c.c. water. Filter, if necessary, and pass in hydrogen sulphide. If there is no action, dilute still more. Result? If the product has the formula Sb_2S_3, write the equation. Treat the antimony sulphide as you did arsenic trisulphide in Experiment XLVIII, *b*.

c. Dissolve half a c.c. of *tartar emetic* in 5 c.c. water, add a drop of hydrochloric acid, and pass in hydrogen sulphide. Result? Conclusion?

d. Heat antimony trioxide (Sb_2O_3) in an ignition tube with charcoal, as you did arsenic trioxide. Results?

EXPERIMENT L.

BISMUTH.

Apparatus. — Mortar and pestle, beaker, test tubes.

Materials. — Bismuth, concentrated nitric and hydrochloric acids, bismuth nitrate crystals, hydrogen sulphide.

a. What is the color of bismuth? Is the metal heavy or light? Malleable or brittle (test with the pestle)? Treat a bit with concentrated nitric acid. Result? Products?

b. To half a c.c. of bismuth nitrate crystals, $Bi(NO_3)_3$, add 5 c.c. water, and shake. Result? If the product has the formula $BiONO_3$, write the equation. Now add hydrochloric acid (concentrated) a drop at a time, heating to boiling after each drop. Result? Use the least possible amount of acid.

c. Put half of the solution from *b* into a beaker, and add much water. Result? Compare with first part of *b*.

d. To the remainder of the acidified solution of bismuth nitrate from *b* add hydrogen sulphide. Result? The visible product is *bismuth sulphide*, Bi_2S_3. Write the equation.

EXPERIMENT LI.

BORAX AND BORIC ACID.

Apparatus. — Platinum wire sealed into glass rod, test tubes, beaker.

Materials. — Borax, potassium dichromate, manganese dioxide, hydrochloric acid, and sodium carbonate (solid).

a. **Borax Bead.** Make a loop 2 mm. in diameter on the end of a platinum wire sealed into a piece of glass tubing. Heat the loop to redness, and dip it into powdered borax, $Na_2B_4O_7 . 10 H_2O$. Heat the adhering borax *just within* the outer edge of the Bunsen flame, at the place *where the flame is widest.* This is the **fusing zone** of the flame. What happens first? Heat until the borax melts to a *transparent* glass. If there is not enough borax to fill the loop, add more, and heat again. This glassy lump is called the **borax bead.**

b. Touch the hot bead to a tiny speck (less than half as large as a pin's head) of *potassium dichromate,* $K_2Cr_2O_7$, and heat at the top of the flame until the dichromate is completely absorbed by the bead. Color? Remove the bead by plunging it while hot into water, and wipe it off the wire.

c. Make a new bead, and touch it to a speck of manganese dioxide. Heat first in the **oxidizing flame** of the burner, *i. e.,* just above the *visible* tip of the flame. Color? Now heat it in the **reducing** region, *i. e.,* just *above* the tip of the *bright blue* interior cone. Heat it there persistently for five minutes, examining it from time to time. Result? Heat it again in the oxidizing flame. Result?

d. **Boric Acid.**—Dissolve 5 grams powdered borax in 10 c.c. hot water, and add 10 c.c. concentrated hydrochloric acid. Set aside until next laboratory period. Result? The product is *boric acid,* H_3BO_3. Filter off the crystals, wash them on the filter with a little cold water, and dry them on fresh filter paper.

e. Dissolve the crystals of boric acid in hot water, and add the solution to a lump of sodium carbonate. Result?

EXPERIMENT LII.

IONIZATION.

Materials. — Solutions of silver nitrate, potassium chloride, potassium chlorate, ammonia, and potassium ferrocyanide; ferrous sulphate crystals.

a. Take 2 c.c. silver nitrate solution in each of two test tubes. To one tube add a few drops of potassium chloride solution. Name the precipitate from Experiment XVI[illegible], *j* to *l*. Equation?

b. To the second tube add potassium chlorate solution. Result? Is the same substance precipitated as in *a*?

c. Powder a crystal of ferrous sulphate, $FeSO_4$, and shake it with 5 c.c. water. Pour off the solution, and add to it a c.c. of ammonium hydroxide solution. Result? If the precipitate is *ferrous hydroxide*, $Fe(OH)_2$, write the equation.

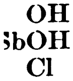
d. To 3 c.c. of *potassium ferrocyanide* solution, $K_4Fe(CN)_6$, add ammonium hydroxide. Result? Is ferrous hydroxide precipitated, as before?

e. Refer to Experiment XXXIX, *a*. Why does the action between sodium bicarbonate and tartaric acid take place only when water is present?

EXPERIMENT LIII.

HYDROLYSIS AND MASS ACTION.

Materials. — Antimony trichloride (crystalline or melted), hydrochloric acid.

a. To a small amount (half a c.c.) of antimony chloride, $SbCl_3$, add 5 c.c. water, and shake. Result? The visible product is essentially *antimony oxychloride*, SbOCl, *i. e.*,  $\overset{OH}{\underset{Cl}{SbOH}}$ *minus* water. Write the equation. Compare the esult with Experiment L, *b*, where bismuth nitrate was used.

b. To the precipitate add concentrated hydrochloric acid, a drop at a time, warming after each drop. Result? If the solution contains antimony chloride, $SbCl_3$, write the equation.

c. Add the solution obtained in *b* to 50 c.c. water. Result? Add concentrated hydrochloric acid again. Result?

d. Compare the equations of *a* and *b*. Write one of them, using, instead of the equality sign, the *double arrow* $\rightleftarrows$. In which direction does the reaction go chiefly when an excess of water is used? When an excess of acid is used?

EXPERIMENT LIV.

SODIUM COMPOUNDS.

Apparatus. — Test tubes, stopper and delivery tube, magnifying glass, platinum wire, watch glass or glass slip.

Materials. — Sodium bicarbonate, lime-water, sodium carbonate (solid and in solution), sodium chloride, calcium chloride, barium chloride, sodium nitrate and sulphate, hydrochloric acid.

a. Refer to Experiment IX for the properties of sodium and its action on water.

b. Heat 2 c.c. powdered sodium bicarbonate carefully in a test tube having a delivery tube that passes into lime-water. Result? Is there any other volatile product? When no more gas is evolved (do not melt the test tube), let the product in the tube cool, and then add 2 c.c. cold water. Note the temperature effect. Compare with this the action of anhydrous sodium carbonate upon water. What are the products formed by heating sodium bicarbonate? Equation?

c. Heat 2 c.c. sodium chloride with 5 c.c. water in a test tube; filter; and let some of the filtrate evaporate completely on a glass slip or a watch glass. Examine the crystals with a magnifying glass, if possible. Their shape?

d. Dissolve a small piece of *calcium chloride*, $CaCl_2$, in 5 c.c. water, and add sodium carbonate solution. Result? Repeat, using *barium chloride* instead of calcium chloride. Result? Write the equations.

e. Dip a platinum wire with a glass holder (*cf.* Experiment LI. *a*) into 5 c.c. concentrated hydrochloric acid in a test tube, and then heat the wire in the Bunsen flame until the flame remains colorless. If necessary, dip the wire more than once. Now wet the clean wire with the acid, dip it into powdered sodium chloride, and heat it. Effect on the flame?

f. Clean the wire and repeat *e*, using sodium nitrate instead of sodium chloride. Repeat again with sodium sulphate. What color do sodium salts give to the flame?

EXPERIMENT LV.

POTASSIUM COMPOUNDS.

aratus. — Watch glass, iron dish, test tubes, beaker or
rating dish, platinum wire, copper wire.
terials. — Potassium chloride, sodium nitrate, sulphur,
n chloride solution, potassium hydrogen tartrate, lime-
dilute sulphuric acid, concentrated hydrochloric acid,
ium nitrate, and potassium sulphate.

Heat 8 grams of potassium chloride and 10 grams of
n nitrate with 20 grams of water until there is com-
solution, and boil off half of the water over the wire
Result? Let the precipitate settle and pour the
on into a test tube. Wash the residue with 5 c.c. cold
and then dissolve it in the smallest possible amount
t water. Pour a few drops of the solution in a watch
and set aside. Result? Compare the crystals with
obtained in Experiment LIV, *c*. Conclusion?
at happens in the test tube containing the original
on? The visible product is *potassium nitrate*, KNO_3.
Mix 3 c.c. powdered potassium nitrate on a clean piece
er with 1 c.c. powdered sulphur, and pour the mixture,
m's length, upon a hot iron dish (use no wire gauze).
t? Let the product cool, boil it with 10 c.c. water in
tube, and add to 5 c.c. of it *barium chloride* solution.
t? See Experiment XXXVI, *b*. What is the product
deflagration of potassium nitrate and sulphur?
Heat an iron dish red hot, and pour upon it 3 c.c. pow-
potassium hydrogen tartrate, $KHC_4H_4O_6$ (cream of

tartar). Results? Color of residue? Heat it five minutes longer at red heat, pressing the mass down with a glass rod occasionally. When the dish is cool, treat the residue in a test tube with dilute sulphuric acid. After all evolution of gas ceases, identify the gas by placing in the mouth of the tube a looped copper wire holding a drop of lime-water. What remains undissolved? What substance would you find in plant ashes if the plants contained potassium salts of organic acids?

d. Clean a platinum wire as in Experiment LIV, *e;* dip it into strong hydrochloric acid, and then into powdered potassium chloride, and heat it in the flame. Result? Repeat, using potassium nitrate instead of the chloride. Use the sulphate. Results? What color do potassium compounds give to the flame?

EXPERIMENT LVI.

SOLUBILITY OF POTASSIUM CHLORIDE.

Apparatus. — Steam bath, water bath, or wire gauze; evaporating dish, balances.

Materials. — Powdered potassium chloride, distilled water.

a. Make a saturated solution of potassium chloride by shaking 12 grams of the powdered substance in a clean flask with 25 c.c. distilled water at the temperature of the room. Continue shaking every little while for fifteen minutes. Record the temperature of the solution, and then weigh out *accurately* into your evaporating dish about 20 grams of the solution. Now evaporate (see *b*) the water until the residual potassium chloride is perfectly dry, and get its weight. From the results calculate how much potassium chloride will dissolve in 100 grams of water at the room temperature.

b. If possible, evaporate the solution of *a* on a steam or water bath. If this is impossible, evaporate slowly and carefully on wire gauze, so as to avoid any loss by spattering.

c. Record your results thus:—

Grams.

Weight of evaporating dish + water + KCl =
Weight of evaporating dish alone =
∴ Weight of water + KCl =
Weight of evaporating dish + KCl =
Weight of evaporating dish alone =
∴ Weight of KCl =
∴ Weight of water found : weight KCl found :: 100 grams : *x*.

EXPERIMENT LVII.

AMMONIUM AMALGAM. DISTINCTIONS BETWEEN THE ALKALI METALS.

Materials. — Ammonium chloride, sodium amalgam, sodium and potassium chlorides, tartaric acid, two unknown substances.

a. Dissolve 2 c.c. ammonium chloride in 5 c.c. water, and add a piece of *sodium amalgam* (Na + Hg). Results? The product is *ammonium amalgam.* Note what happens to it. Odor? Reaction of solution?

Note. — Do not throw away the resulting mercury, but ask what to do with it.

b. Add 5 c.c. water to 3 c.c. powdered potassium chloride and shake thoroughly. Pour off the solution and add to it 5 c.c. of a *concentrated* solution of tartaric acid, $H_2C_4H_4O_6$. Make this by shaking 5 c.c. powdered tartaric acid with 15 c.c. water. Wait for result. Result? The product is *potassium hydrogen tartrate.* Equation?

c. Repeat *b*, using *sodium chloride* in place of potassium chloride. Result? Repeat again, using *ammonium chloride* in place of potassium chloride. Result?

d. From Experiment XXV, *b* and *c*, tell what happens when ammonium salts are treated with alkalies. How distinguish between *sodium* salts on the one hand and *ammonium* and *potassium* salts on the other? Between *sodium* salts and *potassium* salts (two ways)?

e. Get from the instructor two unknown substances, and determine if they are salts of sodium, potassium, or ammonium.

EXPERIMENT LVIII.

CALCIUM.

Apparatus. — Triangle of iron wire, ring stand, blast-lamp, evaporating dish, platinum wire, and coin.

Materials. — Lumps of marble, lime-water, red litmus paper, old mortar, plaster of Paris, paper, calcium chloride, calcium sulphate, and ammonium carbonate solution.

a. Touch a piece of *wet* red litmus paper with a piece of marble. Result? Support a lump of marble about 5 c.c. in volume on a triangle of iron wire laid upon a ring of the ring stand, and heat the marble in the hottest Bunsen flame — in a blast-lamp, if possible. When the marble is cold, touch wet, red litmus with the part that was heated. Result? Explain. What products are formed when marble is heated (*cf.* Experiment XL, *b*)?

Slake about 5 c.c. of quicklime by adding to it water, drop by drop, as long as the water is taken up *readily*. Wait for the result, and describe it. Is there a temperature effect? Equation?

b. To a piece of *old* mortar in a test tube add dilute hydrochloric acid. Identify the gas. What does fresh mortar absorb from the air?

c. Stir 10 c.c. plaster of Paris in an evaporating dish with enough water to form a fairly thick paste. Put the paste upon a piece of paper, and push into it a coin slightly coated with vaseline. At once wash the evaporating dish. Let the paste and coin stand an hour or more. Carefully remove the coin from the plaster. Result?

d. To a solution containing a calcium salt, *i. e.*, calcium *ions*, add *ammonium carbonate* solution. Result? See Experiment LIV, *d.*

e. Clean a platinum wire as in Experiment LIV, *e*, and determine what color *calcium chloride* gives to the flame. Repeat with *calcium sulphate.* Be sure to have concentrated hydrochloric acid upon the wire.

EXPERIMENT LIX.

WATER OF CRYSTALLIZATION IN GYPSUM.

Apparatus. — Evaporating dish, wire gauze, balances.
Material. — Powdered gypsum (*not* plaster of Paris).

a. Weigh your evaporating dish (be sure it is clean and dry), and into it weigh *accurately* about 3 grams of finely powdered gypsum. Get the exact weight of the gypsum taken, and record it.

b. Heat the evaporating dish on a clean wire gauze for ten minutes with the hottest Bunsen flame. Then let the dish cool, weigh it, and record the result. Now heat the dish again for five minutes, let it cool, and determine the weight. Compare the weight after the first ignition with that after the second. Keep your second weight as the final one.

c. Record your results thus: —

Grams.

Weight of evaporating dish + gypsum =
Weight of evaporating dish alone =
∴ Weight of gypsum taken =
Weight of evaporating dish + calcium sulphate =
Weight of evaporating dish alone =
∴ Weight of water found =
∴ Per cent of water in gypsum =

EXPERIMENT LX.

STRONTIUM AND BARIUM.

Apparatus. — Platinum wire and test tubes.

Materials. — Strontium chloride and nitrate, barium chloride and nitrate; solutions of strontium and barium chlorides; ammonium carbonate solution; dilute sulphuric acid.

a. Treat 2 c.c. *strontium chloride* solution with a few drops of ammonium carbonate solution. Result? Repeat, using *barium chloride* in place of strontium chloride. Write equations.

b. Treat 2 c.c. strontium chloride solution with dilute sulphuric acid. Result? See Experiment XXXVI, *a.* Equation?

c. Clean the platinum wire as in Experiment LIV, *e*, and heat a bit of strontium chloride in the flame. Repeat with *strontium nitrate*, $Sr(NO_3)_2$. Results?

d. Repeat *c*, using the corresponding barium salts. Results? How distinguish between calcium, strontium, and barium salts?

EXPERIMENT LXI.

WATER OF CRYSTALLIZATION IN BARIUM CHLORIDE.

Apparatus.—Evaporating dish, wire gauze, balances, air bath (?).

Material.—Barium chloride, chemically pure.

a. Have your evaporating dish clean and dry, and get its weight. Then weigh into it accurately about 3 grams of barium chloride; this should be pure, dry, and finely powdered.

b. Heat the evaporating dish with its contents in an air bath at 120° to 130° C. for one hour, then cool it ten minutes, and get its weight. Record your results as in Experiment LIX, *c*, and get the per cent of water in the crystallized barium chloride.

EXPERIMENT LXII.

MAGNESIUM.

Apparatus. — Tongs, test tubes.

Materials. — Magnesium wire, dilute hydrochloric acid, solutions of magnesium sulphate and chloride, disodium hydrogen phosphate, and ammonium chloride and hydroxide, magnesite.

a. Hold a piece of magnesium wire 2 cm. long in the flame (use tongs). Result? Describe the product.

b. Treat a second piece of magnesium with dilute hydrochloric acid. Result? Identify the gas, and write the equation. See Experiment VI.

c. To 2 c.c. of magnesium sulphate solution add sodium carbonate solution. Result? Repeat, using *magnesium chloride* instead of the sulphate.

d. See Experiment XLVII, *d*, for the action of a solution containing a magnesium salt with disodium hydrogen phosphate and ammonium hydroxide. Rewrite the equations here.

Repeat that experiment with *magnesium chloride* solution instead of the sulphate. Equation?

e. Treat a small piece (half a c.c.) of magnesite with dilute nitric acid. Result? Identify the gas, and write the equation.

From Experiment XL, *b*, tell the effect of heat upon magnesite.

EXPERIMENT LXIII.

ZINC.

Apparatus.—File or sand-paper, knife, iron dish with flat bottom, test tubes, mouth blowpipe.

Materials. —Zinc, tin, lead, and copper ; zinc dust ; solutions of zinc sulphate, sodium hydroxide, and ammonium sulphide ; dilute sulphuric and hydrochloric acids ; hydrogen sulphide ; stick of charcoal.

a. Clean part of a piece of zinc with a file or with sand-paper. Color? Is zinc hard or soft (use a knife or rough edge of glass)? Place a burner below the center of an iron dish. At equal distances from the center place pieces of zinc, tin, lead, and copper, and determine the order in which they *melt.* Return the metals to the proper bottles.

b. Heat a piece of zinc on charcoal with the *oxidizing flame* produced by the mouth blowpipe. Results? To do this proceed as follows:—

Hollow out a depression near one end of the charcoal, and into it put the zinc. To make the blowpipe flame, have a *luminous* Bunsen flame 4 cm. high, and hold the blowpipe so that the flame produced will be inclined about 30 degrees to the horizontal plane.

To make an **oxidizing** flame, hold the end of the blowpipe *inside* the luminous flame, a centimeter above the tip of the dark, inner cone. Hold the charcoal at such a distance that the zinc is in the outer, faintly-luminous part of the blowpipe flame.

To make a **reducing** flame, hold the tip of the blowpipe just at the *outer edge* of the flame at its middle part, and hold the *assay* (here, zinc) much nearer the blowpipe than in the oxidizing flame. The proper region is just at the tip of the *inner, light-blue* cone of the blowpipe flame.

c. What action has hydrochloric acid upon zinc? Equation? See Experiment V for the action of dilute sulphuric acid, and Experiment X for the behavior of *zinc sulphate* crystals, $ZnSO_4 . 7 H_2O$, when heated.

d. Mix 1 c.c. zinc dust with 5 c.c. sodium hydroxide solution, and heat carefully. Test evolved gas with a flame. Result? The solution contains *sodium zincate*, Na_2ZnO_2. Write the equation.

e. To 2 c.c. zinc sulphate solution add a drop of sodium hydroxide solution. Result? What, probably, is the precipitate? Equation? Repeat with a second test tube. Now add to the first tube dilute hydrochloric acid, shaking. To the second tube add an *excess* of sodium hydroxide, shaking. Results? The alkaline solution contains sodium zincate. Equations?

What do these experiments show as to the nature of zinc hydroxide?

f. To 10 c.c. zinc sulphate solution add a drop of dilute sulphuric acid, and then hydrogen sulphide. Result? Put the solution into a beaker and add 5 c.c. *ammonium sulphide* solution, stirring. Result? The product is *zinc sulphide*, ZnS. Color? Equation?

Add 10 c.c. water, stir the mixture, let it settle, and then pour off the *supernatant* liquid. Add 15 c.c. more water, stir, let settle, and *decant*, i. e., pour off the water. This is called "washing by decantation."

To the zinc sulphide add dilute sulphuric acid. Result? What is the gas? Equation? Why was not zinc sulphide precipitated by hydrogen sulphide?

EXPERIMENT LXIV.

EQUIVALENT OF ZINC.

Apparatus. — Same as in Experiment VI.

Materials. — Zinc, in sheet form or in sticks; dilute (5%) sulphuric acid.

a. Dissolve zinc in dilute sulphuric acid just as you did magnesium in Experiment VI, and find the volume of hydrogen liberated by a known weight of zinc. Use from 0.45 gram to 0.55 gram of zinc. If the zinc is in sheet form, it will react readily; but a little impurity, chiefly carbon, will remain insoluble. If the zinc is *pure*, it will react with difficulty; therefore wind about the zinc a piece of platinum wire or a narrow strip of platinum foil. Set the apparatus aside until the zinc is in solution; then proceed as in Experiment VI.

b. Reduce the volume of hydrogen to *standard conditions*, and calculate the *weight* of the hydrogen obtained. Finally, solve for x in the proportion, —

Weight of zinc taken : weight of hydrogen obtained :: x : 1.

The value of x will be the **equivalent** of zinc.

EXPERIMENT LXV.

CADMIUM.

Materials. — Cadmium sulphate, hydrogen sulphide, ammonium sulphide.

a. Dissolve completely not more than 1 c.c. *cadmium sulphate*, $CdSO_4$, in 5 c.c. water, and add hydrogen sulphide *in excess.* Result? The visible product is *cadmium sulphide*, CdS. Color? Equation? What other sulphides of the same color have you had? Wash the precipitate *by decantation*, and treat it with 5 c.c. ammonium sulphide. Result? How distinguish between cadmium sulphide and other sulphides of the same color?

EXPERIMENT LXVI.

MERCURY.

Apparatus. — Pipette (medicine dropper).

Materials. — Mercury, concentrated nitric acid, hydrogen sulphide, hydrochloric acid, sodium hydroxide and potassium iodide solutions, ammonium hydroxide, zinc, and copper.

Caution. — Before working with mercury remove *all rings.* Do not throw mercury away; but ask what you are to do with it.

a. By means of a pipette take from the mercury bottle a globule three times as large as an ordinary water drop; add to it 2 c.c. water and 2 c.c. concentrated nitric acid. Result? Let stand until action stops; this may take some hours.

b. While waiting for *a*, dissolve a globule of mercury the size of a water drop in concentrated nitric acid; this gives *mercuric nitrate*, $Hg(NO_3)_2$. Equation (*cf.* Experiment XXIX, *g*)? Dilute with 15 c.c. water.

c. To 2 c.c. mercuric nitrate solution (*b*) add hydrogen sulphide. Result? The precipitate is *mercuric sulphide*, HgS. Equation?

d. Add to *separate* portions of the nitrate solution, **hydrochloric acid, sodium hydroxide** solution, and **potassium iodide** solution, *respectively.* Results? Add the potassium iodide *drop by drop*, noting changes. Write equations where possible.

Note. — With sodium hydroxide we should expect mercuric *hydroxide*, $Hg(OH)_2$; this, however, decomposes into the *oxide* and *water*.

e. Note the result of *a.* The crystals are *mercurous nitrate*, $HgNO_3$; pour out into a beaker, and add 15 c.c. water and a drop of strong nitric acid.

f. To 2 c.c. of the mercurous nitrate solution of *e* add *hydrogen sulphide.* The precipitate is *mercuric sulphide* and *mercury.* Write the equation.

g. Repeat *d* with the *mercurous* instead of the *mercuric* nitrate. Results? With sodium hydroxide the precipitate is *mercurous oxide*, Hg_2O. Write the equations. Treat the precipitate produced by hydrochloric acid with *ammonium hydroxide.* Result?

h. Into the rest of the mercurous nitrate put a strip of zinc and a copper wire. Results? Now rub them dry. Results?

i. Classify the results of *c*, *d*, *f*, and *g* in five vertical columns.

Formula of Precipitant.	Mercuric Nitrate.		Mercurous Nitrate.	
	Formula of Ppt.	Color.	Formula of Ppt.	Color.
NaOH, etc.				

EXPERIMENT LXVII.

COPPER.

Apparatus. — File or sand-paper.

Materials. — Copper wire, concentrated hydrochloric acid; solutions of cupric sulphate, ammonium hydroxide, sodium hydroxide, and cupric nitrate; grape-sugar; iron nail.

a. File a piece of copper bright. Color? Is it hard or soft? From Experiment LXIII give its *fusibility* compared with zinc, etc. By holding one end of the wire in the flame determine if it is a conductor of heat.

b. From Experiments XXIX and XXXIV tell the action of nitric and sulphuric acids upon copper. Find out if copper reacts readily with concentrated hydrochloric acid.

c. To 2 c.c. cupric sulphate solution add *ammonium hydroxide* solution in excess. Result? Repeat with *sodium hydroxide* instead of ammonium hydroxide. Result? Repeat, having the cupric sulphate *hot*, and then add the sodium hydroxide. Result? The last precipitate is *cupric oxide*, CuO. How formed (*cf.* Experiment LXVI, *d* and *g*)?

d. From Experiment XXXIII, *b* and *c*, tell the effect of hydrogen sulphide upon cupric sulphate. Equation? Pass hydrogen sulphide into cupric nitrate solution. Result? Equation? What is the effect of heating *blue vitriol* (*cf.* Experiment X, *d*)?

e. Dissolve half a c.c. powdered *grape-sugar*, $C_6H_{12}O_6$, in 2 c.c. water, and add it to 5 c.c. cupric sulphate solution. Now add sodium hydroxide solution, shaking, until the precipitate first formed is redissolved. Color? Warm carefully, noting changes. Let stand. Results? Color of product? It is *cuprous oxide*, Cu_2O. What effect had the grape-sugar?

f. Put an iron nail into cupric sulphate solution. Result?

EXPERIMENT LXVIII.

SILVER.

Materials.— Silver foil, silver nitrate solution, nitric acid, sodium thiosulphate; solutions of sodium chloride and potassium bromide, iodide, and cyanide; filter paper; hydrogen sulphide.

a. In a test tube treat a piece of silver foil with 2 c.c. concentrated nitric acid. Result? Equation? Dilute with water to 10 c.c..

b. To 2 c.c. of the solution of *a* add 5 c.c. sodium chloride solution. Result? Equation (*cf.* Experiment XVII, *j*)? Boil the contents of the tube. Result? Get the precipitate on filter paper, and expose it to sunlight. Result?

c. To 5 c.c. of solution *a* add 1 c.c. potassium bromide solution. Result? Heat to boiling, pour off the supernatant liquid, and add to half of the precipitate *sodium thiosulphate* solution, $Na_2S_2O_3$ (make this by dissolving the crystals in water). Result? Expose the other half on filter paper to sunlight. Result?

d. To 1 c.c. silver nitrate solution add 1 c.c. *potassium iodide* solution. Result? Equation?

e. To 1 c c. silver nitrate solution add hydrogen sulphide. Result? Equation?

f. To 1 c.c. silver nitrate solution add *potassium cyanide* solution, drop by drop. Result? Equation? Continue adding it, shaking, until it is in excess. Result? The solution contains the *double cyanide*, KCN. AgCN, *i. e.*, $KAg(CN)_2$. Add sodium chloride solution. Result? Explain the result in terms of the ionic theory (*cf.* Experiment LII).

EXPERIMENT LXIX.

ALUMINUM.

Apparatus. — Test tubes, tongs, blast-lamp.

Materials. — Aluminum wire and filings, white muslin, hydrochloric acid; solutions of sodium hydroxide, aluminum sulphate, sodium carbonate, alum, ammonium hydroxide, and cochineal; powdered alum, sodium bicarbonate, potassium sulphate, ammonium sulphate, aluminum sulphate.

a. Determine whether aluminum is a conductor of heat as in Experiment LXVII, *a.* Does the wire melt in the Bunsen flame (use tongs)? Try the blast-lamp. Result?

b. To 2 c.c. aluminum filings add 5 c.c. concentrated hydrochloric acid, and warm. Result? Test the gas. Equation?

c. Wash the filings remaining from *b*, by decantation, add 5 c.c. concentrated sodium hydroxide solution, and warm carefully. Determine the nature of the gas evolved. Result? The solution contains *sodium aluminate*, Na_3AlO_3 (*cf.* Experiment LXIII, *d*). Equation?

d. To 5 c.c. of *aluminum sulphate* solution, $Al_2(SO_4)_3$, add 1 c.c. sodium hydroxide solution. Result? Equation? Get half of the precipitate into a second test tube, and add an excess of sodium hydroxide solution. Result? If the solution now contains sodium aluminate, Na_3AlO_3, write the equation. To the other half of the precipitate add hydrochloric acid. Result? Equation? Compare with this the behavior of *zinc hydroxide.*

e. Dissolve as much *ammonium sulphate* as possible in 5 c.c hot water, and add to it in a beaker 5 c.c. water similarly saturated with *aluminum sulphate.* Cool the mixture. Result? The product is *ammonium alum.* Heat again to complete solution, and let stand over night. Result? Shape of crystals?

f. Repeat *e*, using *potassium sulphate* instead of ammonium sulphate. Results? Compare the crystals.

g. To 5 c.c. of the solution of any aluminum salt add *sodium carbonate* solution. Result? Identify the escaping gas. The precipitate is *aluminum hydroxide*, $Al(OH)_3$. Mix a cubic centimeter of powdered alum with a cubic centimeter of sodium bicarbonate, and add water. Result?

h. To 1 c.c. of a solution of cochineal add 5 c.c. alum solution, immerse a piece of white muslin, and then add ammonium hydroxide solution, shaking. Results?

EXPERIMENT LXX.

IRON.

Apparatus. — Test tubes, tongs, blast-lamp, magnet, beaker.

Materials. — Iron wire and filings, copper wire; hydrochloric, sulphuric, and nitric acids; solutions of potassium ferrocyanide, ferricyanide, and sulphocyanate; ammonia water, hydrogen sulphide, ammonium sulphide, solid ferrous sulphate, and ferric chloride.

a. Compare the heat conductivity of iron wire with that of copper. Test its magnetic properties; its fusibility in the Bunsen flame and the blast-lamp. Results?

b. Treat 3 c.c. iron filings in a beaker with 20 c.c. dilute hydrochloric acid, stirring. Results? Identify the gas. If the solution contains *ferrous chloride*, $FeCl_2$, write the equation. When action almost ceases, filter off 10 c.c. of the solution. Color of filtrate?

c. Divide the filtrate of *b* into *four* parts. To the *first* add a few drops of *potassium ferricyanide* solution, $K_3Fe(CN)_6$. Result? This is "*Turnbull's blue.*" To the *second* portion add ammonia-water. Result? Equation? Note any change on standing in the air. To the *third* part add *potassium ferrocyanide*, $K_4Fe(CN)_6$. Result? To the last portion add *potassium sulphocyanate* solution, KSCN. Result?

Wash out your test tubes and beakers at once.

d. Filter the remainder of the ferrous chloride solution of *b*, and add 2 c.c. concentrated nitric acid. Heat carefully for two minutes in a beaker. Resulting color? The solution contains *ferric* chloride and nitrate. To a drop of it in a test tube add a drop of potassium ferricyanide solution; if it still gives a blue precipitate, add 2 c.c. more nitric acid, and boil again.

Treat the resulting substance in *four* test tubes with the reagents used in *c*. Result in each case?

The precipitate from potassium ferrocyanide and a ferric salt is "**Prussian blue.**"

e. **Classify the results of *c* and *d* (last part) in five vertical columns.**

Formula of Reagent.	Ferrous Chloride.		Ferric Chloride.	
	Precipitate or Solution?	Color.	Precipitate or Solution?	Color.

f. **In a test tube shake** 2 c.c. powdered *ferrous sulphate* **with 10 c.c. water, pour off** half of the solution, and pass **hydrogen sulphide into it.** Result? Does all the iron **appear to be precipitated?** Write the equation representing **the reaction you would** expect to take place.

From Experiment XXXIII tell the effect of dilute sulphuric acid upon ferrous sulphide. Write the equation here. Compare these two equations. Conclusion?

To the other half of the ferrous sulphate solution add five drops of dilute sulphuric acid, and pass in *hydrogen sulphide*. Compare with the result without the acid? Now add *ammonium sulphide*. Result? Equation?

g. Dissolve 1 c.c. *ferric chloride*, $FeCl_3$, in 10 c.c. water, and pass in hydrogen sulphide at least *two* minutes. Result? Boil the contents of the tube, and then filter. Test the filtrate with a drop of potassium ferricyanide solution. Result and conclusion?

Determine the nature of the residue on the filter paper by collecting it on a piece of porcelain and igniting it. Odor?

Write the equation for the action of hydrogen sulphide on ferric chloride.

EXPERIMENT LXXI.

NICKEL AND COBALT.

Apparatus. — Platinum wire, test tubes.

Materials. — Nickel and cobalt and their nitrates; *solutions* of the nitrates; borax, sodium hydroxide solution, concentrated, chemically pure hydrochloric acid.

a. Give the physical properties of cobalt and nickel from an examination of the metals. Effect of a magnet?

b. To 2 c.c. *nickel nitrate* solution, $Ni(NO_3)_2$, add a drop of hydrochloric acid and then hydrogen sulphide. Result? Now add *ammonium sulphide.* Result? Equation? Explain the results from Experiments XXXIII and LXX, *f.*

c. Make a borax bead as in Experiment LI, *a* and *b*, and determine the color given to it by nickel nitrate.

d. Repeat *b* and *c* with *cobalt nitrate*, $Co(NO_3)_2$, instead of nickel nitrate. Results?

e. To 2 c.c. cobalt nitrate solution add sodium hydroxide solution, a drop at a time, until it is in excess. Results?

f. To 2 c.c. cobalt nitrate solution add 5 c.c. concentrated, chemically pure hydrochloric acid. Result? Dilute with water. Result?

EXPERIMENT LXXII.

MANGANESE COMPOUNDS.

Apparatus. — Platinum wire, test tubes.

Materials. — Manganese sulphate, potassium permanganate, ferrous sulphate, grape-sugar, ammonia-water, hydrogen sulphide, and ammonium sulphide.

a. Dissolve 1 c.c. powdered *manganese sulphate*, $MnSO_4$, in 5 c.c. water. To *half* of it add a drop of dilute sulphuric acid and then hydrogen sulphide. Result? Now add *ammonium sulphide.* Result? Color? Equation? Explain the results.

b. To the other half of solution *a* add ammonia-water. Result? Equation?

c. To 2 c.c. ferrous sulphate solution (*cf.* Experiment LXX, *f*) add potassium permanganate solution. Result? Continue, drop by drop, until the solution is just *faintly* pink. Now add ammonia-water. State and explain the result (*cf.* Experiment XXXIV, *f*).

d. Dissolve a crystal of *potassium permanganate*, $KMnO_4$, in water, and add grape-sugar solution. Result? Explain (*cf.* Experiment LXVII, *e*).

e. From Experiment XVI tell the action of *manganese dioxide* with hydrochloric acid; from Experiment VII, with *potassium chlorate;* from Experiment XLVI, with *hydrogen peroxide;* and from Experiment LI, *a*, tell the color of the *manganese bead.*

EXPERIMENT LXXIII.

CHROMIUM COMPOUNDS.

Apparatus. — Chlorine generator, platinum wire, evaporating dish, test tubes.

Materials. — Solutions of potassium chromate and dichromate, of chromic chloride, of potassium and sodium hydroxides; hydrochloric acid, alcohol, borax, barium chloride solution, chrome-alum.

a. What is the color of solutions of *potassium dichromate* ($K_2Cr_2O_7$), *potassium chromate* (K_2CrO_4), and of *chromic chloride* ($CrCl_3$)?

b. Treat 1 c.c. of *potassium dichromate* solution with a drop of potassium hydroxide solution. Result? From the color tell what is formed.

Complete the equation,

$$K_2Cr_2O_7 + 2\ KOH \longrightarrow ? + ?$$

c. To 1 c.c. *potassium chromate* solution add a drop of concentrated hydrochloric acid. Result? What is formed?

$$2\ K_2CrO_4 + 2\ HCl \longrightarrow ? + ? + ?$$

How can a dichromate be changed to a chromate? A chromate to a dichromate?

d. To 2 c.c. potassium chromate solution add barium chloride solution. Result? Equation? Repeat with *chromic chloride* instead of the chromate. Result?

e. To 1 c.c. chromic chloride solution add a drop of sodium hydroxide solution. Result? Equation? Now add the alkali *in excess*, shaking. Result? The solution contains a *chromite*, $NaCrO_2$. What other elements behave in this way? See Experiments LXIII and LXIX. Save for *g*.

f. Repeat *e* with potassium chromate instead of *chromic chloride.* Result? In what three ways can a chromic salt be distinguished from a chromate?

g. To the clear solution of *e* add *chlorine* gas until there is no further change. Do this in a gas-chamber. Results? Test the resulting solution as in *b*, *c*, and *d*. Results? How can a chromic salt be changed into a chromate?

h. To 10 c.c. potassium dichromate solution in an evaporating dish add 2 c.c. concentrated hydrochloric acid and 2 c.c. ethyl alcohol. Boil until *bright* green, but not to dryness. Test a part of the liquid with barium chloride solution. Result? With potassium hydroxide solution. What does the green solution contain? How can a chromate be changed to a chromic salt? See, also, Experiment XXXIV, *f*.

i. Refer to Experiment LI for the borax bead test. Repeat with a tiny piece of *chrome-alum*. Result?

EXPERIMENT LXXXIV.

LEAD.

Apparatus. — File or knife, test tubes, mouth blowpipe.

Materials. — Lead; hydrochloric, nitric, and sulphuric acids; lead nitrate, solutions of potassium chromate and sodium hydroxide, lead oxide, stick of charcoal.

a. File or cut off the coating on lead. Is it hard or soft? Color? Try to mark on paper with lead. Result? Refer to Experiment LXIII, *a*, for its fusibility. Treat a small piece with hydrochloric acid, both the dilute and the strong. Results? Wash the lead, and add 2 c.c. concentrated nitric acid and 2 c.c. water. Heat gently. Result? Write the equation (*cf.* Experiment XXIX).

b. Heat one-fourth of a c.c. of *lead monoxide* on charcoal in the *reducing* flame (mouth blowpipe). See Experiment LXIII, *b.* Result? How identify the product?

c. Dissolve 2 c.c. powdered *lead nitrate*, $Pb(NO_3)_2$, in 15 c.c. water, heating. Cool, and add to 2 c.c. of the solution 5 c.c. dilute hydrochloric acid. Result? Equation? Wash the precipitate by decantation, and heat it with 10 c.c. water. Result? Cool the solution. Result?

d. To 2 c.c. of the lead nitrate solution add dilute sulphuric acid. Result? Use *potassium chromate* solution instead of sulphuric acid. Result? Equation in each case?

From Experiment XXXIII, *d*, tell effect of *hydrogen sulphide* upon lead nitrate. For the reduction of *lead oxide* by charcoal, see Experiment XL, *a.*

e. To 2 c.c. lead nitrate solution add a drop of *sodium hydroxide* solution. Result? Equation? Now add an excess, shaking. Result? What *three* other hydroxides behaved in the same way? See Experiment LXXIII, *e.*

f. Put into the remainder of the lead nitrate solution a strip of zinc. Leave it *at least* ten minutes. Result? Equation (*cf.* Experiment LXVII, *f*)?

EXPERIMENT LXXV.

TIN.

Apparatus. — Test tubes, stopper and delivery tube, mouth blowpipe.

Materials. — Tin (granular and in a bar); concentrated hydrochloric and nitric acids; solutions of mercuric chloride, stannic chloride, and sodium hydroxide; ammonium sulphide, hydrogen sulphide, zinc, sulphur, stick of charcoal.

a. Treat about 2 c.c. of small bits of tin with 10 c.c. concentrated hydrochloric acid in a test tube. Warm gently to start the action, and when the effervescence is vigorous attach a stopper and delivery tube and collect the gas over water. Identify the gas. Result? The solution contains *stannous chloride*, $SnCl_2$. Equation? Let the action continue at least ten minutes.

b. From Experiment LXIII, *a*, compare the fusibility of tin with that of lead, etc. Hold a bar of tin near your ear, and bend it. Result? What color has bright tin? Is it hard or soft?

c. To 1 c.c. *mercuric chloride* solution, $HgCl_2$, add 4 or 5 c.c. of your stannous chloride solution, and then heat. Note all the changes. The solution contains *stannic chloride*, $SnCl_4$. Equation?

d. To 2 c.c. stannous chloride solution add 5 c.c. water and then hydrogen sulphide. Result? Color? Equation? Wash the precipitate by decantation, and add 5 c.c. *ammonium sulphide* (use an evaporating dish or beaker) and a small lump of sulphur. Warm gently, and stir. Result? Cool, and add dilute hydrochloric acid in excess. Result? Compare the color with that of the original precipitate.

e. To 2 c.c. stannous chloride solution add 1 c.c. concentrated nitric acid, and heat gently. The solution contains *stannic* chloride. Dilute with 5 c.c. water, and pass in hydrogen sulphide. Result? Color? Stannic sulphide is SnS_2. Equation? Wash the precipitate by decantation, add ammonium sulphide and a bit of sulphur, and warm gently. Result? Add an excess of dilute hydrochloric acid. Result? Compare with the color of the original precipitate, and with that obtained at the end of *d.* Conclusion?

f. To 2 c.c. stannic chloride solution add sodium hydroxide solution, drop by drop. Result? Add an excess. Result? What other hydroxides have behaved in the same way? See Experiment LXXIV, *e.*

g. Pour the solution of *a* from any unused tin, and put into it a strip of zinc. Result? Equation? Compare with Experiment LXXIV, *f.*

h. Heat a piece of tin on charcoal in the *oxidizing flame* (mouth blowpipe). See Experiment LXIII, *b.* Results?

EXPERIMENT LXXVI.

COMPOSITION OF CARBON COMPOUNDS.

Apparatus. — Iron dish (sand bath), test tubes, stopper and delivery tube, ignition tube, rubber connector.

Materials. — Sugar, starch, oxalic acid, benzoic acid, powdered cupric oxide, lime-water, gelatine (powdered), soda-lime, urea, litmus.

a. In an iron dish (sand bath) heat one cubic centimeter of *sugar* as long as a change occurs. Repeat with *starch*; with a crystal of *oxalic acid.* Results? What proof have you that the sugar and starch contain carbon? The oxalic acid?

b. Heat half a c.c. of oxalic acid crystals in a test tube. Determine whether carbon dioxide is evolved or not. Results? Heat half a c.c. of *benzoic acid* in a test tube. Result? Is there any evidence of carbon dioxide?

Recall Experiment XL, *a.* Repeat it, using one-fourth of a c.c. of benzoic acid and five times its volume of powdered cupric oxide instead of the charcoal and lead oxide. Results?

Is there any evidence that hydrogen was present in the benzoic acid? What precaution is necessary to be *certain*, if it is known that the cupric oxide used is slightly hygroscopic?

c. Recall Experiment XXV, *a.* Repeat it, using powdered *gelatine* in place of the glue, and powdered *soda-lime* instead of slaked lime. Results? Repeat it again with *urea* in place of the gelatine. Conclusions? If glue and gelatine represent the class of *albumins*, what element must the members of this class contain?

EXPERIMENT LXXVII.

HYDROCARBONS.

Apparatus. — Mortar and pestle, ignition tube 15 cm. long, ring stand, clamp, delivery tube, rubber connector, test tubes, 100 c.c. flask, wire gauze, one-hole stopper, pneumatic trough, evaporating dish.

Materials. — Dry soda-lime and *fused* sodium acetate, lime-water, bromine water, concentrated sulphuric acid, "95 per cent" ethyl alcohol, calcium carbide, benzene.

a. **Methane.** — In a mortar powder and mix 2 grams of soda-lime and 1 gram of dry, fused sodium acetate. With the mixture half fill an ignition tube 15 cm. long, and attach a delivery tube by means of a rubber connector. Support the tube horizontally, tap it to insure a passage for gas, and heat it with a moving flame. Collect the evolved gas — it is impure *methane* (*cf.* § 218) — in three test tubes. Note its physical properties and combustibility. After burning a test tube of the gas, pour lime-water into the tube, close it with the thumb, and shake it. Result? Conclusion? To one test tube of methane add a drop of bromine water. Close the tube, and shake it. Does the color of the bromine disappear?

b. **Ethylene.** — In a 100 c.c. flask *cautiously* add 10 c. c. of concentrated sulphuric acid to 5 c.c. of alcohol. Shake the flask after each addition of acid so as to insure mixing. Support the flask *over* wire gauze but not quite touching it, and attach a stopper and a delivery tube with a rubber connector. *Do not leave the delivery tube in the water when you stop heating!* Heat with a small flame until a regular stream of gas comes off, and collect three test tubes full over water. Note its physical properties and the character of its flame. Test with lime-water and bromine water as in *a.* Results?

c. **Acetylene.** — In a test tube mix 2 c.c. — *no more* — of water with 5 c.c. of alcohol. Add two pieces of *calcium carbide* the size of peas, and at once attach a stopper and delivery tube. Collect the evolved gas (acetylene) over water in three test tubes. Note its properties as directed in *a* and *b*. *Do not inhale it.*

d. **Benzene.** — Put half a cubic centimeter — no more — of *benzene*, C_6H_6, in an evaporating dish. Note its odor. Carefully ignite the benzene. Describe its flame. Write the equation for the combustion of benzene, if the products are carbon dioxide and water.

EXPERIMENT LXXVIII.

ETHYL ALCOHOL.

Apparatus. — Flask (100 c.c.), stopper and delivery tube, test tubes, evaporating dish, distilling apparatus.

Materials. — Molasses (or powdered grape sugar), yeast, lime-water (or baryta water), litmus, sodium bicarbonate, alcohol, powdered shellac or rosin.

a. To 25 c.c. water in a 100 c.c. flask add 5 c.c. molasses or powdered grape sugar and about one cubic centimeter of compressed yeast. Attach tightly a stopper with a delivery tube, and let the tube pass into 5 c.c lime-water or baryta water in a test tube. Let the flask stand in a warm place, and note results. If you leave the delivery tube in the lime-water over night, see that it dips only slightly below the upper surface of the liquid. Why? If the test tube contains no precipitate the next day, heat its contents to boiling. Explain the result. Test the reaction of the solution in the flask toward litmus. Result?

b. Ask the teacher to collect from several students the dilute alcohol they have prepared, and to distill it, if this was not done in connection with § 206. If the first portions of the distillate do not burn when a flame is applied they must be *redistilled.* The first few drops may then be tested for alcohol.

c. Set some of the fermented solution aside, without stoppering the flask, for a week or two. Then note the taste of the solution, its reaction to litmus and its effect upon a little solid sodium bicarbonate in a test tube. Results?

d. Put two or three drops of alcohol into an evaporating dish, warm the dish slightly, and apply a flame. Note the color of the alcohol flame. Write the equation for its combustion.

e. Treat half a cubic centimeter of powdered shellac or rosin in a test tube, with 5 c.c. alcohol. Close the tube with the thumb, and shake it. Result? Add 5 c.c. water. Result? Let the tube stand until the next period. Result?

EXPERIMENT LXXIX.

ETHYL ETHER.

Apparatus. — Evaporating dish, test tubes.
Materials. — Ethyl ether, paraffin.

Caution. *Do not bring the bottle of ether near a flame!*

a. Put two drops of ether into an evaporating dish, remove the ether bottle, and apply a flame to the ether in the evaporating dish. Describe the flame.

b. In a test tube add 2 c.c. ether to a piece of paraffin half the size of a pea, shaking. Result? Pour the ether out into the evaporating dish, and hold the dish in the hand to drive off the ether. Result? Note the volatility and odor of the ether.

EXPERIMENT LXXX.

ALDEHYDES.

Apparatus. — Test tubes, stirring rod, ring stand or rack, tongs.

Materials. — Granular potassium dichromate, concentrated sulphuric acid, methyl alcohol, ethyl alcohol; solutions of silver nitrate, caustic soda, and ammonia; copper wire for spiral.

a. In a test tube add 2 c.c. of concentrated sulphuric acid to 6 c.c. of water, cool the mixture under the tap, and add 2 c.c. of alcohol. Pour this mixture upon 2 c.c. of granular potassium dichromate in a test tube. Hold the test tube over the sink. Results? Note the odor of the escaping vapors of *acetaldehyde*, CH_3CHO. Hold in the vapors a stirring rod wet with *ammoniacal* silver nitrate solution. To make this, add one drop of a 10 per cent solution of caustic soda to 1 c.c. of silver nitrate solution, and then add 1 c.c. of ammonia water. The deposit on the rod is silver. Explain.

b. Put 2 c.c. of *methyl alcohol*, CH_3OH, in a test tube supported in a ring stand or rack. Make a copper spiral by winding about a glass rod or a pencil a foot of copper wire. Remove the pencil or rod, and hold the spiral in the flame (use tongs) until it is red hot. Then drop it into the methyl alcohol. Note the sharp vapor of *formaldehyde*, CH_2O, mixed with the vapor of the alcohol.

$$CH_3OH + O \longrightarrow CH_2O + H_2O.$$

EXPERIMENT LXXXI.

ACETIC ACID AND ACETATES.

Apparatus. — Beaker (50 c.c.), test tubes, evaporating dish, stirring rod, wire gauze, ring stand.

Materials. — Commercial (concentrated and dilute) acetic acid, concentrated sulphuric acid, vinegar, sodium carbonate, litmus and filter papers, alcohol.

a. Note the taste of a drop of *dilute* acetic acid. Heat some to boiling in a test tube. Odor? Its action to litmus? *Cf.* Experiment XVIII, *a* and *b.* Test vinegar in the same ways. Results?

b. In a test tube mix 1 c.c. of concentrated acetic acid with 2 c.c. of alcohol, and add half a c.c. of concentrated sulphuric acid. Heat carefully, and describe the odor. It is that of *ethyl acetate*, $CH_3COOC_2H_5$. The sulphuric acid removes water. Equation? If you were given a liquid suspected of being acetic acid, how would you prove it to be this substance?

c. In a 50 c.c. beaker dissolve 10 grams of sodium carbonate in 10 c.c. of water and add to it commercial acetic acid (5 c.c., or less, at a time) until the reaction is distinctly acid on stirring, and effervescence ceases. Then transfer the solution to an evaporating dish, and concentrate it over the wire gauze until a drop held on a stirring rod crystallizes when cool (*cf.* Experiment XXIX, *g.*) Set the dish aside until the next period. Name the crystals. Their shape? Filter them off, and dry them between filter papers.

d. Carefully heat some of the crystals of *c* in a test tube. Do they contain crystal water (*cf.* Experiment X)? Treat 1 c.c. of them in a test tube, with 1 c.c. of concentrated sulphuric acid, and warm gently. Result? Odor? Remember to pour the concentrated acid *into* water when cleaning the test tube!

To 1 c.c. of the crystals add 1 c.c. alcohol and half a c.c. of concentrated sulphuric acid. Warm gently, and note the odor of the vapors. Result? Conclusion?

EXPERIMENT LXXXII.

OTHER ORGANIC ACIDS.

Materials. — Citric acid, lemon juice, oxalic acid, benzoic acid, alcohol, sodium bicarbonate, potassium permanganate solution, dilute and concentrated sulphuric acid, litmus.

a. For the properties of *tartaric acid* see Experiments XVIII, *c;* XXXIX, *a;* LV, *c;* and LVII, *b* and *c*.

b. Make an aqueous solution (by heating) of 1 gram, or less, of crystallized *citric acid,* $H_3C_6H_5O_7 + H_2O$, and note its taste, odor, and reaction toward litmus and toward sodium bicarbonate. Repeat, using *lemon juice* instead of citric acid solution. Results?

c. See Experiment LXXVI for the behavior of *oxalic acid,* $H_2C_2O_4$, when heated. Prove the presence of crystal water in oxalic acid. To 1 c.c. of potassium permanganate solution add half a c.c. of dilute sulphuric acid and then oxalic acid solution, drop by drop. Result? Conclusion?

d. Heat 1 c.c. of *benzoic acid,* C_6H_5COOH, with 5 c.c. of water. Result? Boil for a moment. Odor of vapors? Now cool the solution under the faucet. Result? Redissolve the benzoic acid by applying heat. Cautiously taste a drop of the solution, and note its action toward litmus and sodium bicarbonate. Results?

In a test tube heat carefully 1 c.c. of benzoic acid with 1 c.c. of alcohol until you get a solution; then add half a c.c. of concentrated sulphuric acid and heat again. Note the odor of the vapors of *ethyl benzoate,* $C_6H_5COOC_2H_5$.

Pour the solution into 10 c.c. water, and note the separation of the oily ester.

EXPERIMENT LXXXIII.

SOAP.

Apparatus. — "Tin" can, stirring rod, test tubes, ring stand.

Materials. — Sodium hydroxide, lard, fine salt, "Castile" or "Ivory" soap, litmus, dilute sulphuric acid, calcium sulphate solution.

a. In a clean "tin" can dissolve 8 grams of sodium hydroxide in 60 c.c. cold water. If possible have the cover only partially cut out, so that it may be pushed down as a lid during the boiling. To the alkaline solution add 25 grams of *lard*, and heat the mixture to boiling, having the opening of the can almost closed by the lid. *Be careful not to let the alkali spatter into your eyes!*

After 30 minutes *stop the boiling*, and see if the mixture begins to become solid. (Care!) If not, continue heating until it does.

Now add to the mixture, while it is still warm, 16 grams of fine salt in lots of about 2 grams each. Stir *carefully* after each addition. Finally, boil the mixture for ten minutes, and let it cool. The soap will appear as a solid cake on the surface of the solution. Remove it, rinse it with a little water, and let it dry.

b. Dissolve about 1 c.c. of "Ivory" or "Castile" soap in 10 c.c. of water, and test the reaction of the solution with litmus. Result? Treat half of the solution with dilute sulphuric acid. Result? The solid product is a mixture of the organic acids of the soap.

Treat the other half of the soap solution with a solution of calcium sulphate. Result? Heat to boiling. The product is the calcium salt of the acids ("lime soap"). (*Cf.* §§ 43, 366, and 387.)

EXPERIMENT LXXXIV.

CARBOHYDRATES.

Apparatus. — Beaker, test tubes, ring stand, wire gauze.

Materials. — Fehling's solution (see *a*), grape sugar, cane sugar, molasses, concentrated hydrochloric acid, sodium carbonate, starch or starch paste.

a. See Experiment LXVII for the action of grape sugar with alkaline cupric salts. A better solution for testing the sugars is the one called "**Fehling's Solution.**" Cupric sulphate crystals (34.64 grams) and 1 c.c. dilute sulphuric acid are dissolved in water, and the solution is diluted to exactly 500 c.c. This is solution I. Solution II consists of 175 grams of sodium potassium tartrate, 50 grams of sodium hydroxide, and enough water to make the volume exactly 500 c.c. These solutions are kept in separate, rubber-stoppered bottles. Equal volumes of the two are mixed just before they are used. One cubic centimeter of Fehling's solution is completely reduced by exactly 0.005 gram of grape sugar.

To 10 c.c. Fehling's solution in a beaker add a drop of a solution of grape sugar, and heat to boiling over the wire gauze. Result? Let the precipitate settle, and add another drop of grape sugar solution; repeat the process until the Fehling's solution has just lost its blue color. Calculate how much grape sugar you added.

b. In a test tube add some cane sugar solution to 5 c.c. Fehling's solution, and heat to boiling. Is there reduction? Try a solution of molasses instead of cane sugar. Result?

c. To 20 c.c. cane sugar solution in a beaker add 2 c.c. of concentrated hydrochloric acid, and heat gently to boiling for 15 minutes over the wire gauze. Cool, and neutralize the acid with solid sodium carbonate; then test with Fehling's solution. Result?

d. Repeat *b* and *c*, using 20 c.c. starch solution (make it as in Experiment XLIV, *d*) instead of cane sugar. Results?

EXPERIMENT LXXXV.

SOME PRINCIPLES OF QUALITATIVE ANALYSIS.

Apparatus. — Funnel, funnel support, beaker, test tubes.

Materials. — Solutions of nitrates of iron (ferric), silver, copper, barium, and sodium; hydrochloric acid, hydrogen sulphide, dilute sulphuric acid, ammonia water, filter papers, and two or more "unknown" substances.

a. Qualitative Analysis is a system of experiments for the separation and identification of the elements present in mixtures of substances. In a limited sense the term is applied to the detection of the ordinary metals and acids. The separation of metals present as *ions* in a solution is possible if we can convert some of the metals into insoluble compounds while leaving the others in solution. The following experiments show how a scheme of analysis may be devised for the separation of the five metals: *silver*, *copper*, *iron*, *barium*, and *sodium*. We use solutions of the *nitrates*, since these are all soluble. Make *ferric nitrate*, if this is not found in the laboratory, by covering about 1 gram of iron wire or filings with 10 c.c. of water in a beaker and adding 10 c.c. dilute nitric acid in small portions. When action ceases, filter the solution and dilute it to 60 c.c.

b. To 5 c.c. of each of the nitrates named in *a* add dilute *hydrochloric acid* — one cubic centimeter at a time — until there is an *excess*. To know if you have an excess of the precipitant let the precipitate settle, and add a drop more of the precipitant to the clear solution; or filter a little of the precipitated solution and test the filtrate in the same way. (*Cf.* § 355, *last two paragraphs.*) Be sure that your test tubes are clean for every test.

Copy the following table in your note book, and put down the results in their places.

Effect of	$AgNO_3$	$Cu(NO_3)_2$	$Fe(NO_3)_3$	$Ba(NO_3)_2$	$NaNO_3$
HCl					
H_2S					
H_2SO_4					
NH_4OH					

c. Treat 5 c.c. of each of the solutions named in *a* with hydrogen sulphide in excess. Make sure you have an excess, as suggested in *b*. Tabulate your results. Be sure the tube delivering the gas is clean before every test. For the action of hydrogen sulphide with ferric salts, *cf.* Experiment LXX, *g*. For the conversion of *ferrous* ions into the *ferric* state, see Experiment LXX, *d*.

d. Treat 5 c.c. of each of the five solutions with an excess of dilute sulphuric acid, and tabulate the results.

e. Repeat *d*, using ammonium hydroxide solution in place of sulphuric acid.

f. From the results tabulated in *b* to *e* devise a plan for identifying any one of the five nitrates, and of separating them, if they are all present in a mixture.

g. From previous experiments tell how you would determine whether a white, soluble solid given you was sodium *chlorate*, *nitrate*, *sulphate*, *carbonate*, *sulphite*, *acetate*, or *thiosulphate*?

h. If you wished to make a mixture of copper and barium salts, would you use copper *sulphate*? Why? Why not use barium *chloride* or ferric *chloride* solution if you wish to get a soluble mixture of the ions of these metals and those of silver?

i. Get from the teacher two or more unknown substances, and determine what metal or metals of the five named are present; also what acid.

EXPERIMENT LXXXVI.

QUANTITATIVE COMPOSITION OF MAGNESIUM OXIDE.

Apparatus. — Evaporating dish, 50 c.c. beaker, watch glass, evaporating apparatus (*cf. b*), tongs.

Materials. — Magnesium wire or ribbon, concentrated nitric acid.

a. In a weighed porcelain evaporating dish weigh out accurately about 0.5 gram of magnesium wire or ribbon. Transfer it to a 50 c.c. beaker provided with a watch glass, and add to it, in several portions, 6 c.c. of concentrated nitric acid diluted with 12 c.c. of water. When the magnesium has dissolved, transfer the solution, without loss, to the evaporating dish, rinsing the watch glass and beaker with 10 c.c. of water as directed in Experiment XV, *b*.

b. Evaporate the solution of magnesium nitrate (on a water bath or steam bath if possible; otherwise on a wire gauze) until the residue is syrupy. Be careful to avoid loss. Further evaporation *over* a flame generally causes spattering; but the heating may be continued safely if the flame is applied from above. Do this as follows:

Hold the evaporating dish by means of iron or brass tongs grasped in the left hand, and carefully move the dish about, so that the syrupy liquid is spread in a thin layer over the sides of the dish, but not nearer to the edge than *one centimeter*. At the same time hold the Bunsen burner in the right hand, move the flame gently round and round, and direct it upon the contents of the dish. By careful manipulation the magnesium oxide may be obtained as an opaque powder. When the decomposition of the nitrate seems complete, apply the flame from below again. Heat the dish to faint redness for five minutes, cool it, and get its weight. Record your weights as in Experiment XV, *d.*

c. Solve the following proportion for *x*: weight of magnesium used : weight of oxygen united with the magnesium :: **equivalent** of magnesium (found in Experiment VI, *f*) : *x*. Result? What relation exists between the oxygen that united with a given weight of magnesium and the hydrogen replaced by the same weight of magnesium?

APPENDIX.

TABLE OF EQUIVALENTS IN ENGLISH AND METRIC UNITS.

A. Length.

1 centimeter = 0.3937 in.
1 decimeter = 10 cm.
1 meter = 100 cm. = 1,000 mm.
1 meter = 39.37 in. = 3.28 ft.
1 kilometer = 1,000 m. = 0.6214 mile.

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1 inch = 2.54 cm.
1 foot = 0.3048 m.
1 mile = 1.6094 km.

B. Area.

1 sq. cm. = 0.155 sq. in.
1 sq. m. = 10.764 sq. ft. = 1.196 sq. yd.
1 sq. km. = 0.385 sq. mile.

C. Volume.

1 cu. cm. = 0.061 cu. in.
1 cu. m. = 35.315 cu. ft.
1 liter = 1,000 cu. cm. = 1.0567 qt. (U. S.)

D. Weight.

1 gram = 15.4324 grains.
1 kilogram = 1,000 grams = 2.2046 lbs.
1 grain = 0.0648 gram.
1 ounce (avoirdupois) = 28.35 grams.
1 ounce (troy) = 31.1 grams.

TABLE OF ATOMIC MASSES AND SPECIFIC HEATS.

		Atomic Masses.*			Specific Heats.
		Clarke.		Richards.	
		H = 1.	O = 16.	O = 16.	
Aluminum	Al	26.9	27.1	27.1	0.214
Antimony	Sb	119.5	120.4	120.0	0.0508
Argon	A	39.6	39.96	39.92	
Arsenic	As	74.45	75.0	75.0	0.0814
Barium	Ba	136.4	137.40	137.43	
Bismuth	Bi	206.5	208.1	208.0	0.0308
Boron	B	10.9	11.0	11.0	0.366
Bromine	Br	79.35	79.95	79.955	0.0843†
Cadmium	Cd	111.55	112.4	112.3	0.0567
Cæsium	Cs	131.9	132.9	132.9	
Calcium	Ca	39.8	40.1	40.1	0.170
Carbon	C	11.9	12.0	12.001	0.459††
Cerium	Ce	138.0	139.0	140.	0.0448
Chlorine	Cl	35.18	35.45	35.455	
Chromium	Cr	51.7	52.1	52.14	0.100
Cobalt	Co	58.55	59.00	59.00	0.107
Columbium	Cb	93.0	93.7	94.	
Copper	Cu	63.1	63.60	63.60	0.0952
Erbium	Er	164.7	166.0	166.	
Fluorine	Fl	18.9	19.05	19.05	
Gadolinium	Gd	155.2	156.4	156. ?	
Gallium	Ga	69.5	70.0	70.0	0.079
Germanium	Ge	71.9	72.5	72.5	
Glucinum	Gl	9.0	9.1	9.1	0.058
Gold	Au	195.7	197.2	197.3	0.0324
Helium	He	3.93	3.96	3.96	
Hydrogen	H	1.000	1.008	1.0075	
Indium	In	113.1	114.0	114.	0.0570
Iodine	I	125.89	126.85	126.85	0.0541
Iridium	Ir	191.7	193.1	193.0	0.0326
Iron	Fe	55.5	55.9	55.9	0.114
Krypton	Kr	81.15	81.76	81.7	
Lanthanum	La	137.6	138.6	138.5	0.0449
Lead	Pb	205.36	206.92	206.92	0.0314
Lithium	Li	6.97	7.03	7.03	0.941
Magnesium	Mg	24.1	24.3	24.36	0.250
Manganese	Mn	54.6	55.0	55.02	0.122
Mercury	Hg	198.50	200.0	200.0	0.0319†

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* Table of Atomic Masses, prepared by Prof. F. W. Clarke; "Journal of the American Chemical Society," Vol. XXIV, No. 3; March, 1902.

† Solid. †† Diamond.

TABLE OF ATOMIC MASSES AND SPECIFIC HEATS.— ***Continued.***

		Atomic Masses.			Specific Heats.
		Clarke.		Richards.	
		H = 1.	O = 16.	O = 16.	
Molybdenum	Mo	95.3	96.0	96.0	0.0722
Neodymium	Nd	142.5	143.6	143.6	
Neon	Ne	19.8	19.94	19.94	
Nickel	Ni	58.25	58.70	58.70	0.108
Nitrogen	N	13.93	14.04	14.04	
Osmium	Os	189.6	191.0	190.8	0.0311
Oxygen	O	15.88	16.000	16.00	
Palladium	Pd	106.2	107.0	106.5	0.0593
Phosphorus	P	30.75	31.0	31.0	0.189*
Platinum	Pt	193.4	194.9	195.2	0.0324
Potassium	K	38.82	39.11	39.14	0.166
Praseodymium	Pr	139.4	140.5	140.5	
Rhodium	Rh	102.2	103.0	103.0	0.0580
Rubidium	Rb	84.75	85.4	85.44	
Ruthenium	Ru	100.9	101.7	101.7	0.0611
Samarium	Sm	149.2 ?	150.3 ?	150.0	
Scandium	Sc	43.8	44.1	44.	
Selenium	Se	78.6	79.2	79.2	0.0762†
Silicon	Si	28.2	28.4	28.4	0.203†
Silver	Ag	107.11	107.92	107.93	0.0570
Sodium	Na	22.88	23.05	23.05	0.293
Strontium	Sr	86.95	87.60	87.68	
Sulphur	S	31.83	32.07	32.065	0.178††
Tantalum	Ta	181.5	182.8	183.	
Tellurium	Te	126.5	127.7	127.5 ?	0.0474
Terbium	Tr	158.8	160.	160.	
Thallium	Tl	202.61	204.15	204.15	0.0335
Thorium	Th	230.8 ?	232.6 ?	233.	0.0276
Thulium	Tm	169.4	170.7	171. ?	
Tin	Sn	118.1	119.0	119.0	0.0562
Titanium	Ti	47.8	48.15	48.17	0.1485
Tungsten	W.	182.6	184.	184.	0.0334
Uranium	Ur	237.8	239.6	238.5	0.0277
Vanadium	V	51.0	51.4	51.4	
Xenon	Xe	127.	128.0	128.	
Ytterbium	Yb	171.9	173.2	173.	
Yttrium	Y	88.3	89.0	89.0	
Zinc	Zn	64.9	65.4	65.40	0.0955
Zirconium	Zr	89.7	90.4	90.6	0.0662

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*Yellow. † Crystalline. †† Rhombic.

TENSION OF AQUEOUS VAPOR IN MM. OF MERCURY (REGNAULT).

TEMP.	TENSION.	TEMP.	TENSION.	TEMP.	TENSION.
0° C.	4.6	11° C.	9.8	21° C.	18.5
1	4.9	12	10.4	22	19.7
2	5.3	13	11.1	23	20.9
3	5.7	14	11.9	24	22.2
4	6.1	15	12.7	25	23.6
5	6.5	16	13.5	26	25.0
6	7.0	17	14.4	27	26.5
7	7.5	18	15.4	28	28.1
8	8.0	19	16.3	29	29.8
9	8.5	20	17.4	30	31.6
10	9.1	...	...	...	...

TABLE OF SPECIFIC GRAVITIES (WATER = 1).

Acetic acid *	1.053	Lead	11.35
Alcohol (ethyl) * . . .	0.794	Limestone	3.2
Aluminium	2.67	Lithium	0.59
Antimony	6.72	Magnesium	1.74
Arsenic	5.7	Manganese	7.2 to 8
Bismuth	9.8	Mercury †	13.596
Boron	2.63	Nickel	8.57
Brass	8.3	Nitric acid (conc.) * .	1.42
Carbon (gas)	1.8	Phosphorus	1.83
Carbon disulphide * . .	1.27	Platinum	21.5
Chloroform *	1.5	Potassium	0.865
Coal (anthracite) . . .	1.36 to 1.8	Silicon	2.49
Cobalt	8.8	Silver	10.57
Copper	8.9	Sodium	0.97
Diamond	3.53	Sulphur	2.05
Ether *	0.72	Sulphuric acid . . .	1.84
Glass	2.6 to 3.6	Tin	7.29
Gold	19.3	Water at 0° C. . . .	0.999
Hydrochloric acid (conc.) *	1.2	— — 4.0° C. . .	1.000
Ice	0.918	— — 100° C. . .	0.958
Iodine	4.95	— (sea)	1.026
Iron	7.8	Zinc	6.9 to 7.2

* At 15° C. † At 0° C.

WEIGHT (IN GRAMS) OF A LITER OF THE DRY GAS AT 0° C. AND 760 MM.

Air	1.293	Marsh gas	0.717
Ammonia	0.762	Nitric oxide	1.34
Carbon dioxide	1.977	Nitrogen	1.256
Carbon monoxide . . .	1.251	Nitrous oxide	1.97
Chlorine	3.18	Oxygen	1.429
Hydrochloric acid . .	1.64	Sulphur dioxide . . .	2.87
Hydrogen	0.0896	Steam	0.806
Hydrogen sulphide . .	1.542		

Table III.—100 C.C. OF A GAS, AT THE TEMPERATURES AND PRESSURES GIVEN, REDUCED TO 0° C. AND 760 MM.

TEMP.	PRESSURE IN MILLIMETERS OF MERCURY.										
	720	725	730	735	740	745	750	755	760	765	770
15° C. . .	89.79	90.42	91.04	91.67	92.29	92.91	93.54	94.16	94.78	95.41	96.03
16° . . .	89.48	90.11	90.73	91.35	91.97	92.59	93.21	93.83	94.45	95.08	95.70
17° . . .	89.17	89.79	90.41	91.03	91.66	92.27	92.89	93.51	94.13	94.75	95.37
18° . . .	88.87	89.48	90.10	90.72	91.34	91.97	92.57	93.19	93.80	94.42	95.04
19° . . .	88.57	89.18	89.79	90.41	91.03	91.66	92.26	92.87	93.48	94.10	94.71
20° . . .	88.26	88.87	89.48	90.10	90.72	91.34	91.94	92.55	93.16	93.78	94.39
21° . . .	87.96	88.57	89.18	89.79	90.41	91.02	91.63	92.24	92.85	93.46	94.07
22° . . .	87.66	88.27	88.87	89.48	90.10	90.72	91.31	91.93	92.53	93.14	93.75
23° . . .	87.36	87.97	88.57	89.18	89.79	90.41	91.00	91.61	92.22	92.82	93.43
24° . . .	87.07	87.67	88.27	88.87	89.48	90.09	90.69	91.31	91.91	92.51	93.11
25° . . .	86.78	87.38	87.98	88.58	89.19	89.79	90.39	91.00	91.60	92.20	92.80

Table IV. — List of the Metals in the Order of Decreasing Solution Tension.

The Alkali Metals.
The Alkaline-Earth Metals.
Magnesium.
Aluminum.
Manganese.
Zinc.
Cadmium.
Iron.
Cobalt.
Nickel.
Tin.
Lead.
Hydrogen.
Bismuth.
Antimony.
Copper.
Arsenic.
Mercury.
Silver.
Palladium.
Platinum.
Gold.

The metals appearing first in the table can replace those that follow, in the solutions of their salts.

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